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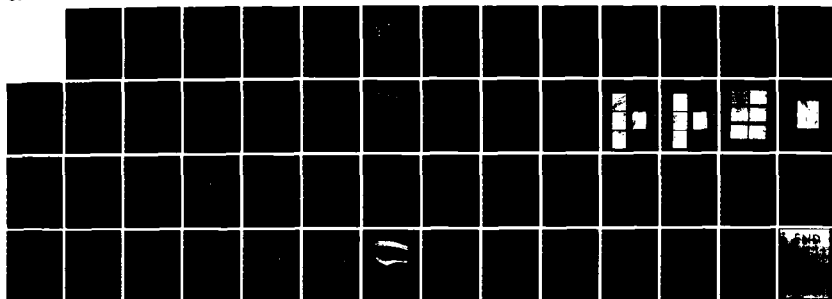
INVESTIGATION OF CHEMICAL DURABILITY MECHANISMS IN  
FLUORIDE GLASSES(U) CATHOLIC UNIV OF AMERICA WASHINGTON  
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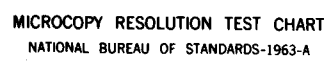
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Investigation of Chemical Durability  
Mechanisms in Fluoride Glasses

by

Catherine J. Simmons and Joseph H. Simmons

ABSTRACT

*Zirconium tetrafluoride*

Aqueous corrosion mechanisms are investigated in heavy-metal fluoride glasses. The family of glasses based on the  $ZrF_4$  glass former is rapidly attacked by water which is either unbuffered or contains acidic components. However, these glasses resist corrosion by basic solutions.  $ThF_4$ -based glasses exhibit a higher resistance. Comparisons are made between the 2 glass families; pH dependence of corrosion is analyzed and a corrosion model is presented.

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# Investigation of Chemical Durability Mechanisms in Fluoride Glasses

by

Catherine J. Simmons and Joseph H. Simmons

## I. Introduction

Fluoride glasses are rapidly becoming strategic materials because of their optical performance at visible and infrared wavelengths.<sup>1</sup> In the area of bulk optics (lenses, filters and windows) and in the area of optical communications (optical fibers and integrated optics components) fluoride glasses promise to extend the range of characteristics presently available. Fluoride glasses benefit from 2 major differences from the traditional silicate based optical components. These are: (1) an extended range of optical transparency covering both the visible regions and the IR region with negligible absorption levels out to at least 7 $\mu$ m, and (2) a lower melting temperature, rarely reaching above 900-1100°C. In addition to applications in IR optics, their IR transparency has made them desirable for optical communications since the expected Rayleigh loss is greatly reduced at long wavelengths. Calculated Rayleigh scattering losses near the minimum absorption region for these glasses are far below silicates at values near 0.01dB/km.<sup>1</sup> Research in fibers and optical components has been intensive and short fiber lengths have been produced with losses near 6dB/km.<sup>2</sup>

Fluoride glasses, however, have 2 major problems: One of fabrication because of ready crystallization and one of use due to their high susceptibility to chemical attack. The first detailed measurements of fluoride glass dissolution in water were reported by C. Simmons at the 1st International

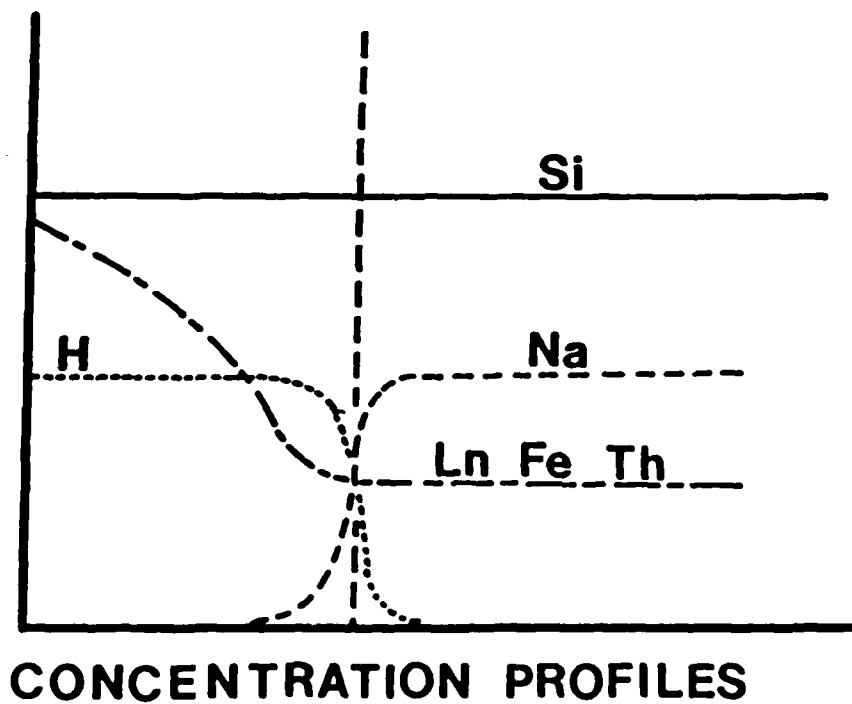
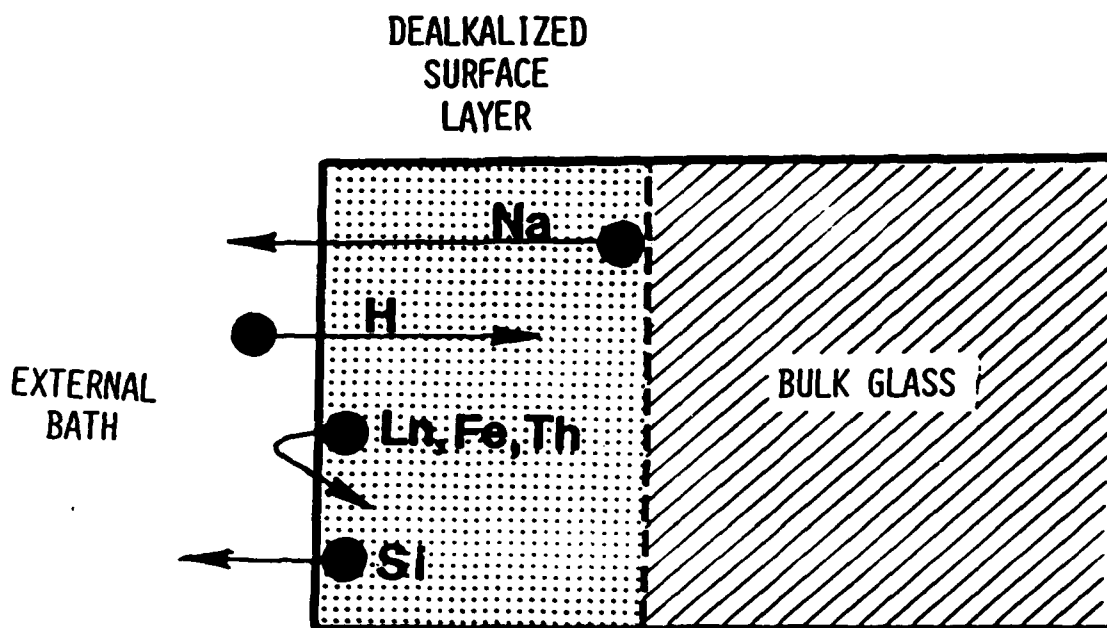
Symposium on Halide glasses in 1982<sup>3</sup> and in Ref. 4. Since then, we have conducted research on the chemical durability of halide glasses under this ONR contract, with the main goals of: (1) characterizing the chemical resistance or dissolution of this new class of glasses, and (2) determining the mechanisms which control their chemical behavior in aqueous solutions. The results of our research during the first year are described here, and were presented at the following conferences: (1) Second International Symposium on Halide glasses held in Troy, N.Y., August 1983<sup>5</sup> and (2) Annual Meeting of the American Ceramic Society held in Pittsburgh, PA, May 1984.<sup>6</sup>

In discussing the results of our research on the processes controlling the chemical durability of fluoride glasses, it is best to do so in the context of the established framework for the analysis of silicate glass corrosion. Rather than refer to numerous reviews on the subject, some of which are the authors' own,<sup>7</sup> we decided to highlight the important concepts in the following section: Chemical Durability Processes in Silicate Glasses.

## II. Chemical Durability Processes in Silicate Glasses

The chemical durability of glasses is controlled by a variety of competing mechanisms. Silicate glasses, whose aqueous leaching mechanisms have been studied for several decades, are fairly well understood. These glasses leach under the control of alkali ion exchange processes and silica dissolution. In general, positively charged ions in water (protons or hydronium  $H_3O^+$  ions) diffuse into the glass and ion exchange with alkali ions present in the initial glass composition. With the passage of time, a de-alkalized region is formed in the glass at the interface with the soaking solution (see Fig. 1). For common glass compositions, as the thickness of the de-alkalized region grows,

FIGURE 1 -- MECHANISM OF LAYER FORMATION IN SILICATE GLASSES



LAYER FORMATION IN SILICATES

the interdiffusion and ion-exchange process slows down sufficiently so that the de-alkalization process is no longer rate controlling.

The initial de-alkalization process plays a major role in the determination of the material's leaching characteristics. If the de-alkalized layer is dense and inhibits the interdiffusion process, then durability is generally high, since the competing mechanism of matrix dissolution is limited to the glass surface, and silica dissolution is generally a slow process. In durable glasses, the de-alkalized layer protects the interior from chemical attack and drastically slows down corrosion. However, if the de-alkalized layer is porous, so that the matrix is more accessible to aqueous attack, the glass will exhibit a lower chemical durability. In fact, in some glasses, the layer is so porous, that it plays no part in slowing down chemical attack. The layer structure, therefore, controls the chemical behavior of the glass after the initial de-alkalization stage. In glasses with high alkali content, pH run away effects are observed during de-alkalization leading to very high pH (10 to 11) at the solution-glass interface, which, in turn, leads to much higher silica dissolution rates.

Other mechanisms of chemical corrosion generally break down into the effect of external conditions on the balance between de-alkalization and chemical dissolution. For example,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ ,  $\text{CaO}$  generally increase the durability of silicate glasses because (1) they release their cation in a form which precipitates or adsorbs in the de-alkalized layer thus slowing down the interdiffusion necessary for de-alkalization to occur.

The effect of pH of the soaking solution also simplifies to a competition between de-alkalization and dissolution. In general silicate glasses are most durable in solutions of neutral pH values. At high pH values, de-alkalization



is slowed down, and silica dissolution is accelerated, so that the glass dissolves quickly while receiving reduced protection from the de-alkalized layer. Silicate glasses undergo accelerated corrosion at high pH values. At low pH values, de-alkalization is accelerated but the protective role of the layer is generally reduced due to structural changes in the layer. Chemical corrosion is generally increased when reducing solution pH below the range pH 6-pH 8. However, basic solutions are generally worse than acidic solutions.

Recent research on the behavior of nuclear wastes vitrified in silicate glasses has also shown the effect of the de-alkalization/dissolution balance in stagnant solutions.<sup>8</sup> When the glass volume or exposed surface area is large or comparable to the solution volume, and solution replenishment is slow or non-existent, pH drift conditions occur. In silicate glasses it is found that as de-alkalization occurs, alkali leaching products from the glass form hydroxides which are highly basic as protons are removed from solution. If the soaking solution is not sufficiently buffered to neutralize these hydroxides, then the pH of the solution increases, in turn accelerating chemical corrosion. This process can continue until the glass is dissolved completely, or until the solution becomes saturated in some of the major components of the glass, at which point the dissolution rate is reduced to the rate of precipitation of that component from the saturated solution. Often, the pH run-away process is arrested when a buffering component (phosphoric, boric or silicic acid) is released into the solution at a concentration high enough to establish an equilibrium pH.

### III. ONR Contract Research

The research program followed during the first year of the ONR sponsored project consisted of 3 major undertakings:

- (a) A study of conditions, apparatus and analysis techniques for the measurements of corrosion rate;
- (b) Measurements of the corrosion behavior of fluoride glasses from a wide variety of families of composition using (1) the chemical analysis of the soaking solution, (2) the measurement of the rate of release of individual components, (3) IR transmission and reflection spectroscopy and (4) microscopy using an SEM instrument and surface analysis using an electron-probe;
- (c) Interpretation of results with the goals to develop an understanding of the mechanisms which control chemical corrosion and to develop models for predicting the behavior of classes of fluoride glasses under various use conditions. Combined together these investigations would lead to a better selection of materials for the various DoD applications and, more importantly, to a definition of conditions for their use.

#### A. Leaching Test Definition

One of the major results of the intense study of the behavior of vitrified nuclear wastes in aqueous solutions was that differences in leaching test conditions led to different results and interpretations. This result was followed by the finding that few laboratories either control or understand the conditions of their leach tests.

In our study, we followed the lesson learned in our work on the leaching mechanisms of nuclear waste glasses, and adapted our test conditions to those

found useful in the previous study. For example, we used the same de-ionized water for the soaking solution as was certified by the MCC (Materials Characterization Center for Nuclear Waste Isolation) round-robin analysis.<sup>9</sup> The water is purified by using a modified filtration and ion exchange system available from Millipore, Inc. which treats the water with a reverse osmosis filter, 2 ion exchangers, 2 charcoal cartridges and a 0.2 $\mu$  filter. The latter is essential for removal of contaminated elements from the previous cartridges. The containers were 200ml PMP (polymethylpentene) vessels found to be inert in aqueous solutions over a wide range of pH values and up to 95°C. When solid samples were used, they were supported by Teflon baskets prewashed to remove residues from the Teflon. The soaking solutions were analyzed with a DC Plasma Spectrometer and an Atomic Absorption Spectrometer calibrated daily with certified standards.

Solutions used for soaking the samples were either de-ionized water or buffered solutions. Several methods were tested when buffered solutions were used: (1) commercial buffers using simple acids, and organic acids, and (2) manual dispensation of HCl or NaOH. Most tests were conducted using several methods to detect any effect due to the buffer solutions. Solution volumes were selected to be large compared to sample area, and soaking times were kept short so that the effect of an accumulation of corrosion products was minimized. Our tests, however, showed that due to a tendency for the corrosion products to fail to mix completely in the solution, their reaction with the glass is not easily avoided and must be considered as an important part of an on-going corrosion process. This behavior will be discussed with the results. When powders were used as test samples, constant stirring was maintained to minimize variations in corrosion product concentrations in the solution.

Finally, in our solution analyses, we attempted to determine anionic content by either fluoride electrode measurements, pH measurements, ion concentration analysis using a Dionex Ion Analyzer, or titration measurements. A comparison of these measurements with the cation concentration measurements in an attempt to reach ionic charge balance in solution contributed greatly to the formation of an overall leaching model for fluoride glasses, as will be seen below.

Our research on surface analysis was limited to IR transmission and reflection measurements, and to scanning electron microscopy with x-ray microanalysis due to a lack of surface analysis instrumentation at Catholic University. At our present location (University of Florida), in addition to a Fast Fourier Transform IR Spectrometer with hot stage and 2 SEM with x-ray microprobes, we have available a 200keV TEM, an ESCA/SIMS instrument and a scanning Auger Spectrometer. Therefore in the upcoming phase of our research, we expect to strengthen our proposed mechanisms with structural and surface composition measurements.

#### B. Measurements of the Corrosion Behavior of Fluoride Glasses

Corrosion behavior measurements were conducted on a wide variety of glass compositions which fell into 3 families of glasses: Zr-based or Hf-based glasses, Thorium-based glasses and glasses based on trivalent and divalent cations. This section is therefore divided into:

- 1) Measurements on  $ZrF_4$ -based glasses
- 2) pH studies on  $ZrF_4$ -based glasses
- 3) Measurements on other glasses.

## 1. Measurements on ZrF<sub>4</sub>-Based Glasses

Tests of chemical durability were conducted on solid samples of ZrF<sub>4</sub>-based glasses provided by a number of laboratories as shown in Table 1. Tests were conducted in de-ionized water to measure the rate of release of various components from the glass. IR measurements and SEM observations of tested samples allowed an evaluation of surface characteristics. Tests were also conducted by subjecting solid samples to various conditions of relative humidity to assess the effect of storage in air on proposed optical components. Once the leaching characteristics of bulk samples were determined, measurements were conducted on powder samples for comparison and to determine their usefulness, since powder samples require a smaller sample volume and allow more tests to be conducted.

### a. Aqueous Solution Tests

#### (1) Leaching

Figure 2 shows the testing system which consists of a 250ml PMP container filled with sufficient de-ionized water to yield a ratio of 100ml volume/cm<sup>2</sup> of sample surface area. The sample is polished on all sides using a 6μ diamond paste in Halocarbon oil (water and oxygen free halogen based oil) and cleaned in Toluene. The sample is supported on a Teflon basket in the test container (see Fig. 2). The Teflon basket is cleaned as described in MCC Test Specification in order to avoid the release of metal impurities and HF from the Teflon.<sup>9</sup> The samples are soaked in the water for periods of 30 minutes to 5 days. The entire solution is replaced at each analysis interval. Solution analysis was conducted as shown in Table 2 with calculated accuracy shown in

**TABLE 1 COMPOSITION**  
(mole %)

**GROUP I**

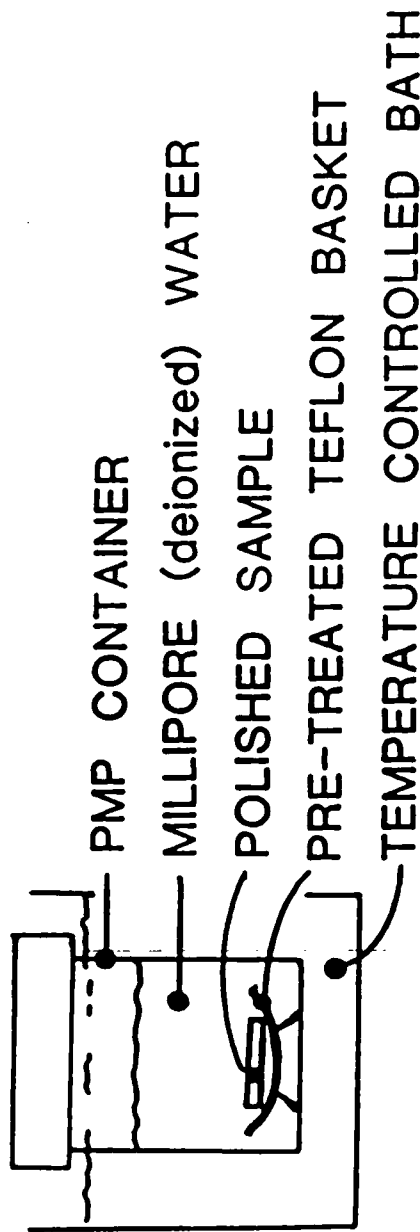
	ZrF <sub>4</sub>	BaF <sub>2</sub>	LaF <sub>3</sub>	AlF <sub>3</sub>	LiF	NaF	PbF <sub>2</sub>	Source
ZBL	62	33	5	.....	.....	.....	.....	
ZBLA	58	33	5	4	.....	.....	.....	R.P.I.
ZBLAN	54.0	15.0	6.0	4.0	.....	21.0	.....	
ZBLAL	51.8	20.0	5.3	3.3	19.6	.....	.....	
ZBLALP-1	50.2	19.3	5.1	3.1	18.9	.....	3.4	N.R.L.
ZBLALP-2	50.4	15.5	4.9	3.1	20.2	.....	4.9	

**GROUP II**

	BaF <sub>2</sub>	ZnF <sub>2</sub>	LuF <sub>3</sub>	YbF <sub>3</sub>	ThF <sub>4</sub>	NaF	Source
BZLT	19	27	27	.....	27	.....	R.A.D.C.
BZYbT	19	27	.....	27	27	.....	
BZYbTN	10	27	.....	27	27	9	R.P.I.

FIGURE 2

# EXPERIMENTAL PROCEDURE



## SOLUTION ANALYSIS METHODS:

D C PLASMA	A.A.	ION CHROMATOGRAPHY
Al, Ba, La, Lu, Na, Pb, Th, Yb, Zn, Zr	Li	F <sup>-</sup> , Cl <sup>-</sup>

$$\text{Leach Rate} = \frac{\text{ppm} \bullet \text{sol. vol.}}{\text{surface area} \bullet \text{time}}$$

## TABLE 2 DETECTION LIMITS

**D.C. Plasma: Al = 3 ppb Pb = 60 ppb**

**Ba = 25 "      Th = 50 "**

**La = 30 "      Yb = 60 "**

Lu = 50 "      Zn = 20 "

**Na = 4 "      Zr = 75 "**

**Atomic Absorption: Li = 30 ppb**

**Ion Chromatography:  $F^- = 5 \text{ ppb}$**

**$\text{Cl}^- = 10 \text{ ppb}$**



Table 2. Leach tests in de-ionized water were conducted on the glass compositions shown in Table 1. These samples were obtained from a variety of laboratories also shown in Table 1.

Figures 3 through 6 show the results of leach tests conducted at room temperature on the following glasses respectively: ZBL, HBL, ZBLA and ZBLAL. The results showed little difference between the corresponding leach rates, and, with the exception of La, there was little difference between the rates of leaching of the individual components. After an initial short time period, the glasses appeared to undergo nearly congruent leaching. Unlike silicate glasses, the leach rate of Al was generally higher than the Zr. However, as in silicates, the alkalis, Li, leached at a higher rate than the Zr, although, in contrast to silicates the differences are small. In all compositions, the leach rate decreased as a function of time, coming down by nearly a decade in 5 days. The pH of the solution was observed to drift rapidly during the tests from an initial value of pH 5.7, in de-ionized water, to a final value between 3.1 and 4.

Tests were conducted to determine the equilibrium pH of the ZBLAL glass in de-ionized water. Samples were prepared with large glass surface area to solution volume ratios and allowed to leach for several days until the solution pH remained constant. The equilibrium value proved to be pH 2.46.

## (2) Infrared Measurements

A series of infrared spectroscopy studies was conducted to determine the effect of aqueous corrosion and surface layer formation on the IR transmission capabilities of fluoride glasses. The results (Fig. 7) show the formation of a large absorption peak, centered at  $2.9\mu\text{m}$  ( $3400\text{cm}^{-1}$ ) due to  $\text{OH}^-$

FIGURE 3

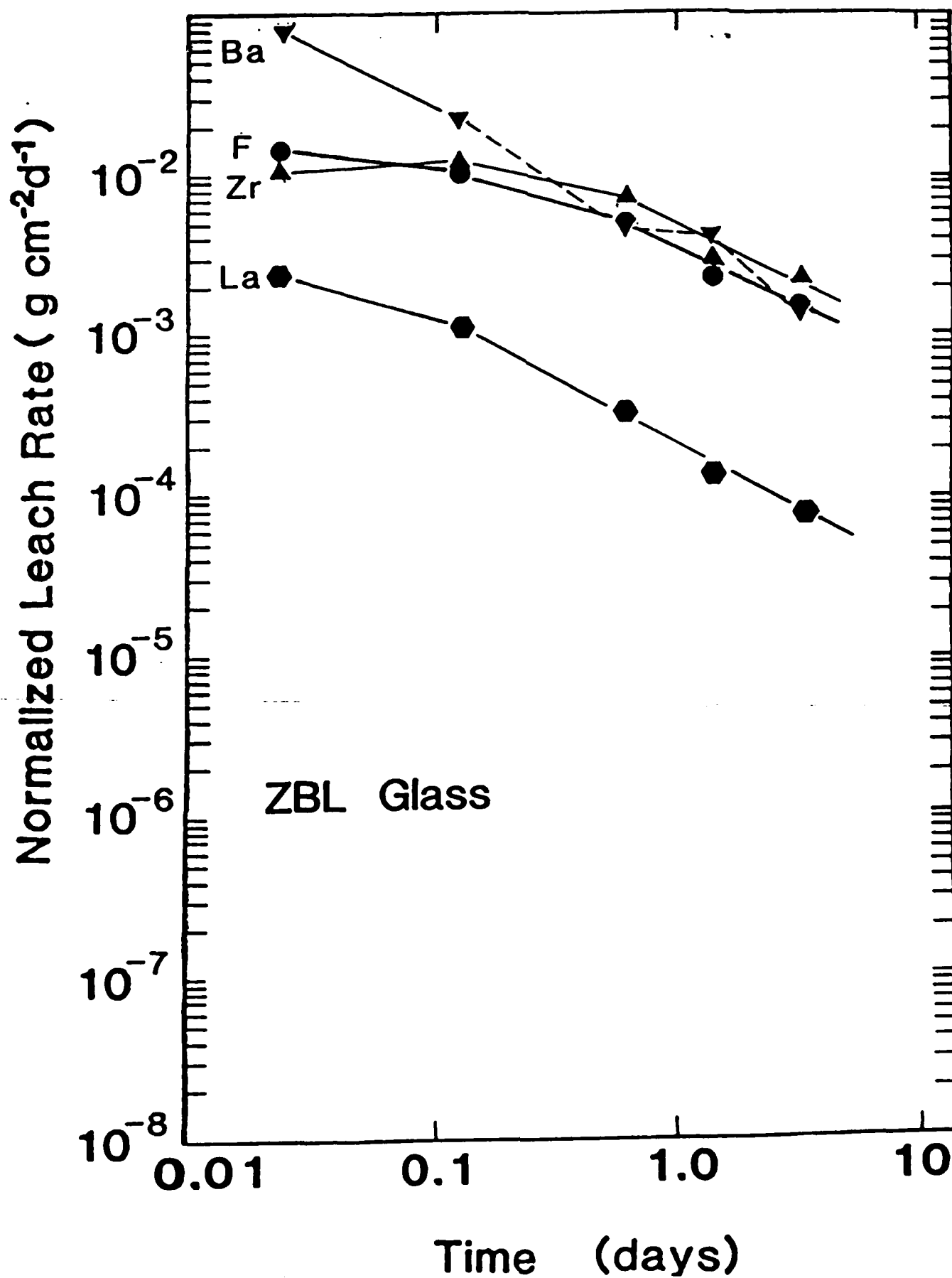


FIGURE 4

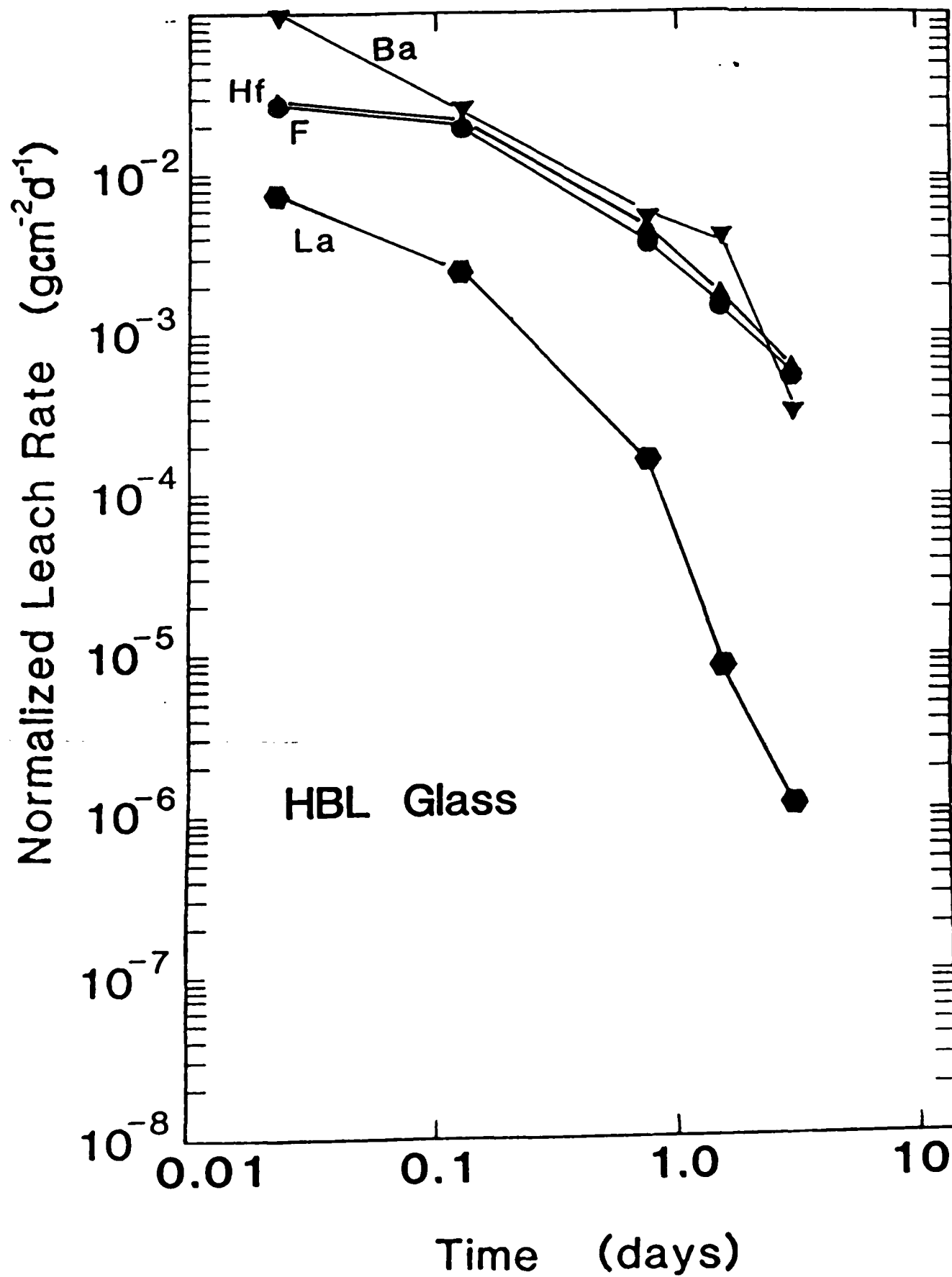


FIGURE 5

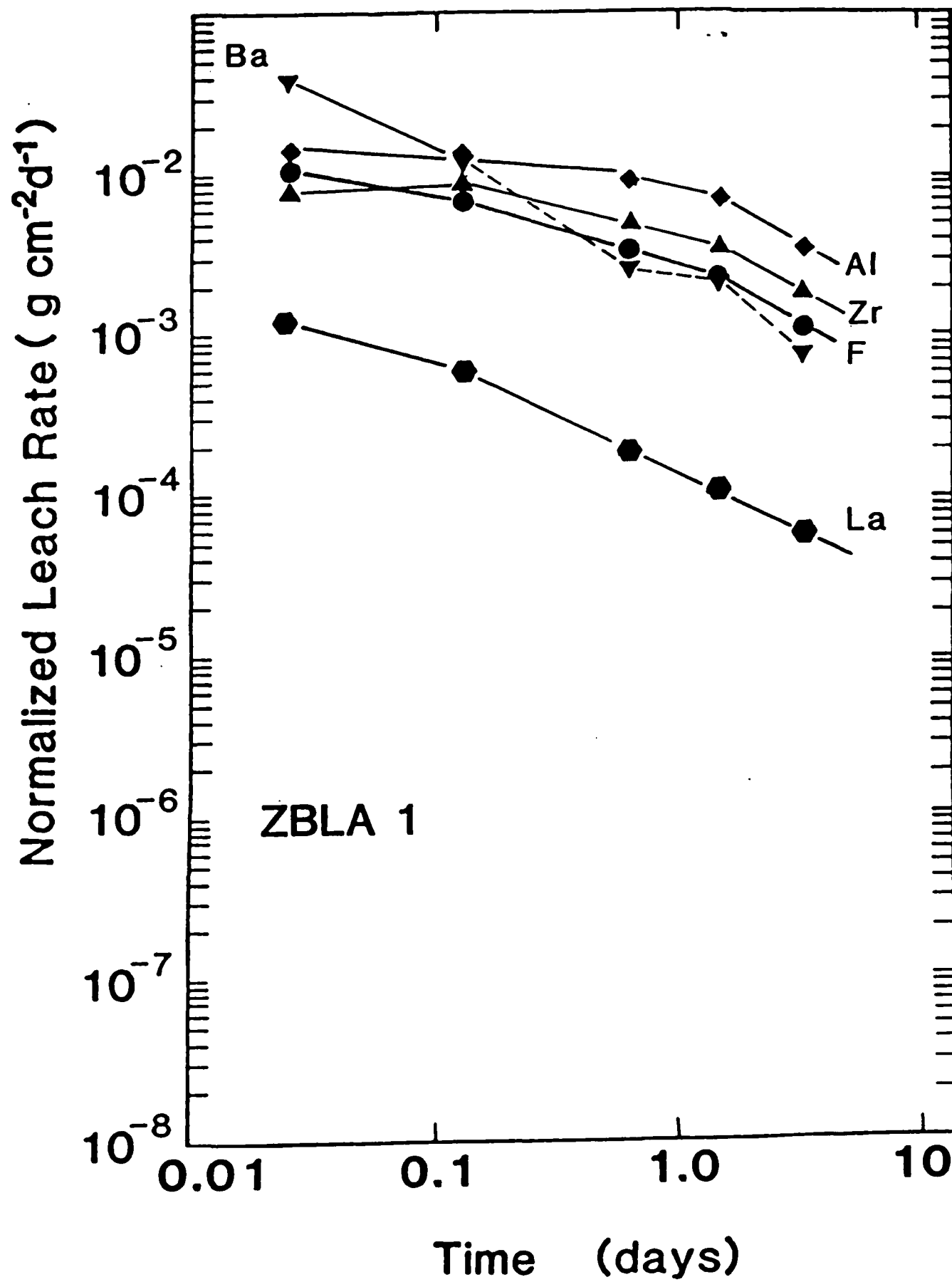
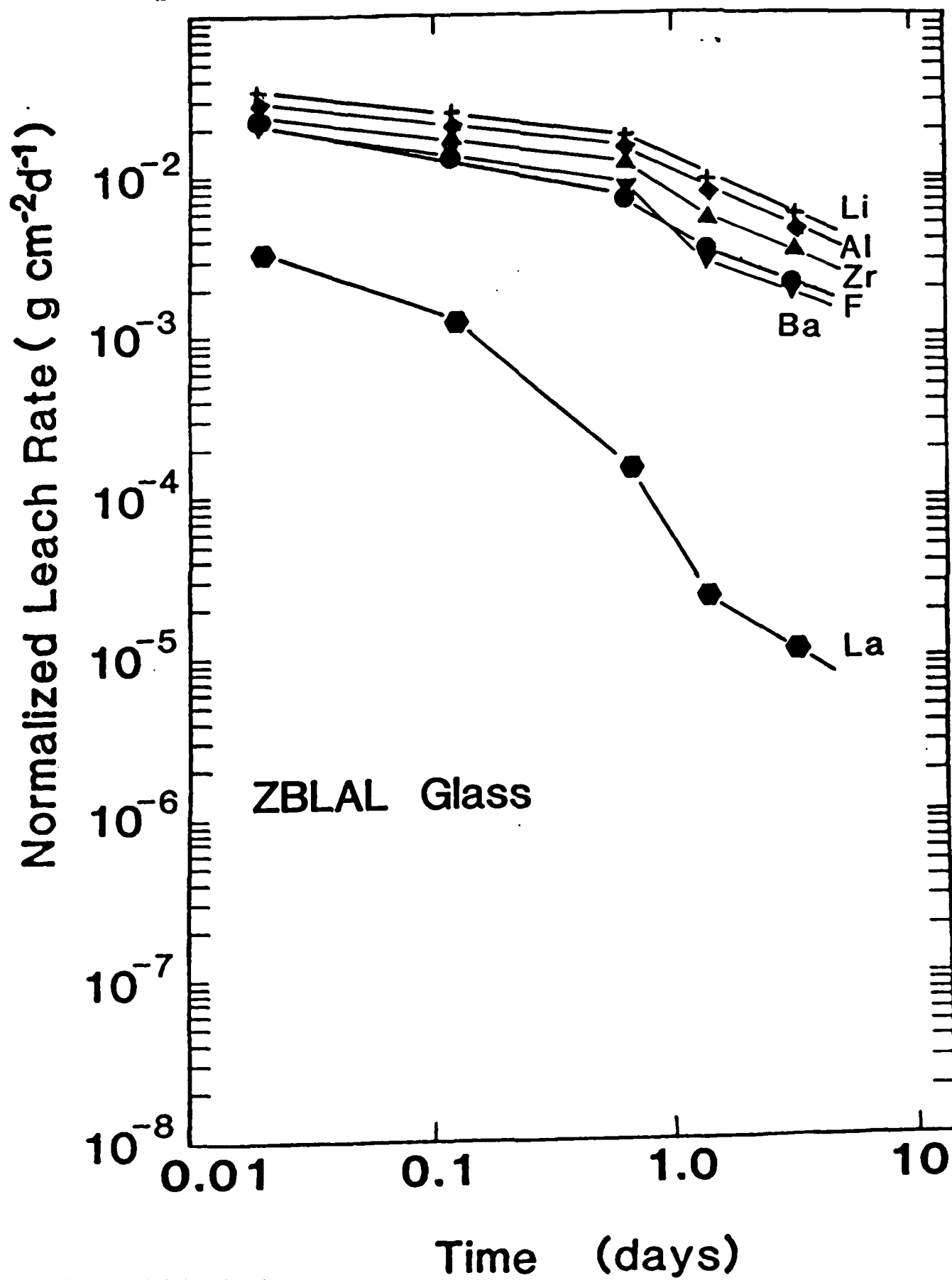
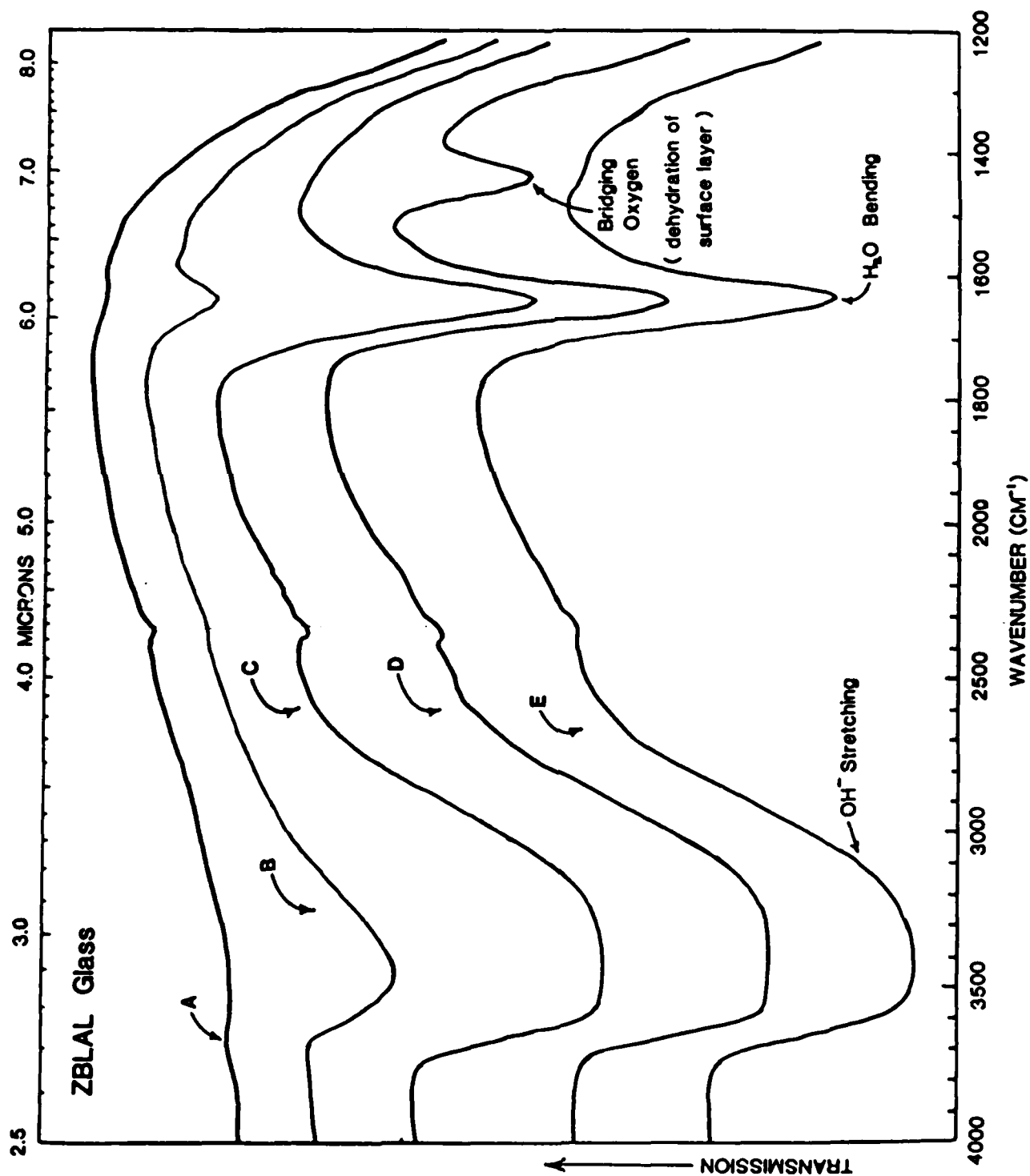


FIGURE 6



stretching vibrations, and a second absorption at  $6.1\mu\text{m}$  ( $1640\text{cm}^{-1}$ ), attributed to HOH bending vibrations. In addition, a third absorption band at  $7\mu\text{m}$  ( $1440\text{cm}^{-1}$ ) was observed when the samples were dried. It was felt that this could be due either to the formation of oxide complexes in the surface layer or the presence of carbonates formed by dissolved  $\text{CO}_2$  in the water.

In order to eliminate one of these alternatives, a systematic study was performed in which a sample was exposed to a variety of environmental conditions. Curve A in Fig. 7 represents the spectra obtained when the sample was successively exposed at  $80^\circ\text{C}$  to (1) vacuum for 21 hours, (2) a partial atmosphere of pure  $\text{CO}_2$  gas for 2 hours, (3) 100% relative humidity (RH) for 2.5 hours, and (4) 100% RH with  $\text{CO}_2$  gas for 20 hours. No liquid water was allowed to condense on the sample during this test. No changes were observed in the spectra. The sample was then soaked for 1 hour (Curve B) and 4 hours (Curve C) in water which had been freed of  $\text{CO}_2$  by boiling and purging with  $\text{N}_2$ . The formation and growth of the absorption bands at  $2.9\mu\text{m}$ , due to  $\text{F}^-/\text{OH}^-$  anion exchange causing surface hydration, and at  $6.1\mu\text{m}$ , due to surface adsorbed water was observed. There was no sign of an absorption at  $7\mu\text{m}$ . The sample was then dried in vacuum at  $30^\circ\text{C}$  for 42 hours, causing dehydration of the surface layer and giving rise to the  $7\mu\text{m}$  band (Curve D). Finally, the sample was soaked in water saturated with  $\text{CO}_2$ . Within 1 hour, the  $7\mu\text{m}$  absorption peak had nearly vanished (Curve E), proving conclusively that this absorption is due to oxide formation, and further, that it is a bridging oxygen, since it does not appear in the spectra of samples known to contain hydroxyl groups. Our results confirm the conclusions reported by Drexhage and co-workers<sup>10</sup> that the absorbance shoulder observed at  $7\mu\text{m}$  in some of their glasses is due to the presence of oxide impurities in some of their melts.



**FIGURE 7-IR Measurements on ZBLAL Glass Corroded in Deionized Water**

The IR reflection spectra taken during our study show a strong metal-fluoride peak at  $\sim 17\mu\text{m}$  ( $600\text{cm}^{-1}$ ) in the polished sample which gradually disappears as leaching progresses and hydration of the surface layer occurs.

### (3) Electron Microscopy

Soaked samples exhibited surface deposits (Figs. 8-10) which were studied by scanning electron microscopy and x-ray micro analysis using a wavelength dispersive spectrometer. ZBL, HBL, ZBLA and ZBLAL samples were analyzed. All samples exhibited precipitated crystals over the entire surface. Below the precipitated crystals, the glass surface was heavily hydrated and cracked over a depth of tens to hundreds of microns. No protective de-alkalized layer, commonly seen in silicates, was observed. The hydrated surface layer readily cracked away from the bulk, and where pieces had peeled off (possibly during leaching), further chemical attack and cracking was observed, extending into the glass. The profile view of the sample surface seen in Fig. 8 shows that the hydrated surface layer produced by 5 days of leaching at room temperature was approximately  $150\mu\text{m}$  thick. The crystalline deposits covering the surface of the samples were analyzed by EPMA to contain large amounts of Zr or Ba as shown in Fig. 11, with each crystal exhibiting a distinct structure. The Zr crystals were needle-like, while the Ba crystals appeared as spherulites composed of very thin parallel plates (see Figs. 8 and 11). These crystalline deposits result from a saturation of the aqueous solution at the glass solution interface which was caused by the stagnant conditions of these tests. It appears that saturation and precipitation occur rapidly, before the corrosion products have an opportunity to diffuse into the main body of the solution. Similar deposits have been observed by Doremus et. al. and x-ray analysis has indicated that they are  $\text{ZrF}_4$  crystals.<sup>11</sup>



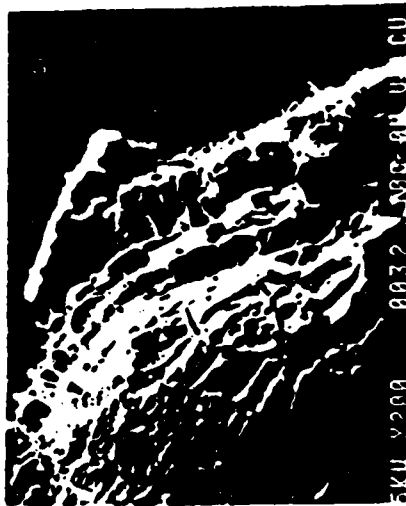
# **SURFACE STRUCTURE AFTER LEACHING 5 DAYS AT 25 C**



**Precipitated  
Crystal Deposits**



**Dehydrated Surface Layer**



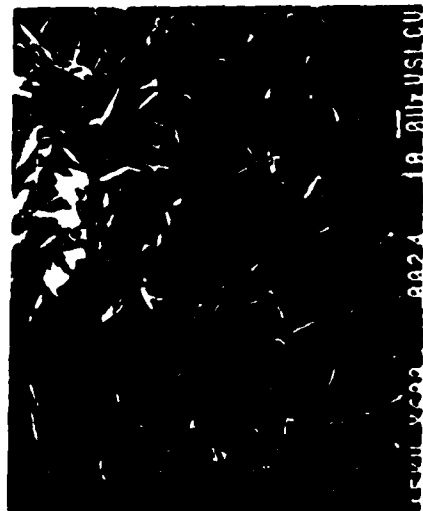
**Cross-Section  
of Surface Layer**



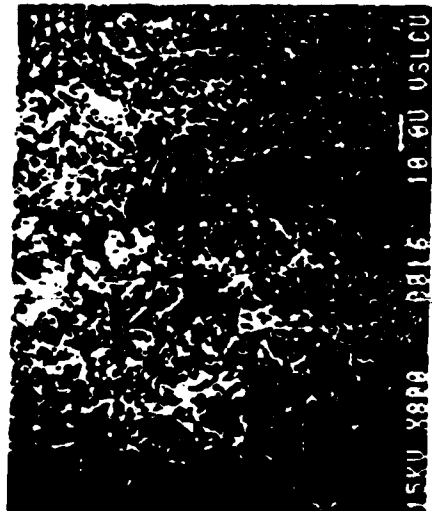
**Two Types of Crystals**

**FIGURE 8**

# **SURFACE STRUCTURE OF HBL AFTER LEACHING FOR 5 DAYS AT 25 C**



**Precipitated  
Crystal Deposits**



**Porous, Hydrated, Crystalline,  
Thin, Protective Surface Film  
Leached Layer**



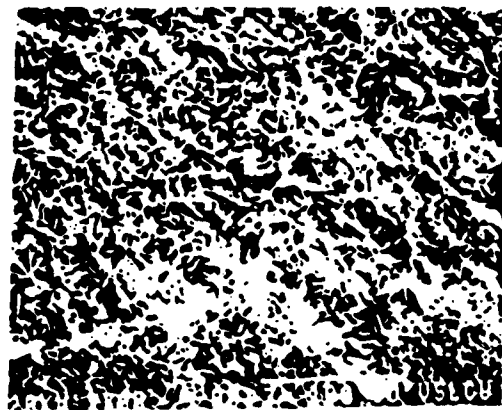
**- peeling**



**Bulk Glass Has Tiny Surface Cracks**

**FIGURE 9**

# ZBLAL



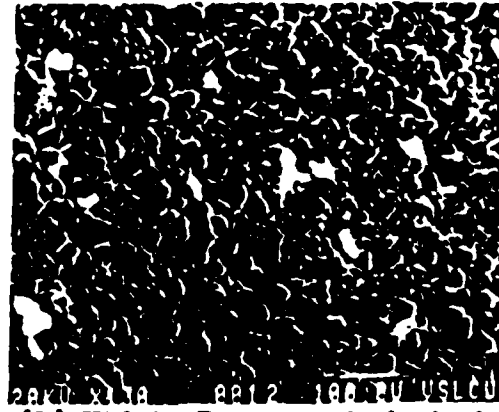
(A) Precipitated  
Crystal Deposits



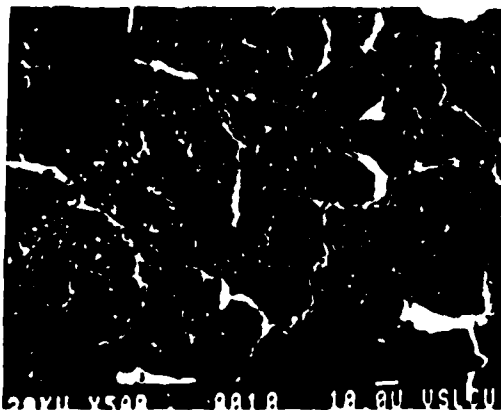
(B) Porous, Hydrated Layer  
- Cracked



(C) Porous, Hydrated Layer



(D) Thick, Porous, Hydrated  
Layer With Cracks



(E) Same As (D) With  
Piece Removed



(B) Bulk Glass Has Many  
Small Cracks

**FIGURE 10**

FIGURE 11 -- BA AND Zr SURFACE CRYSTAL DEPOSITS



#### b. Humidity Tests

The leach tests showed a rapid chemical dissolution of the glass when soaked in water. However halide glass samples have been observed to remain relatively uncorroded in ambient atmosphere for long time periods, up to several months. Other investigators have reported extensive corrosion and the appearance of a thick white crust in tests conducted in 100% relative humidity. The conditions of these tests allowed for a variation in temperature which could easily cause condensation of liquid water on the sample surface.

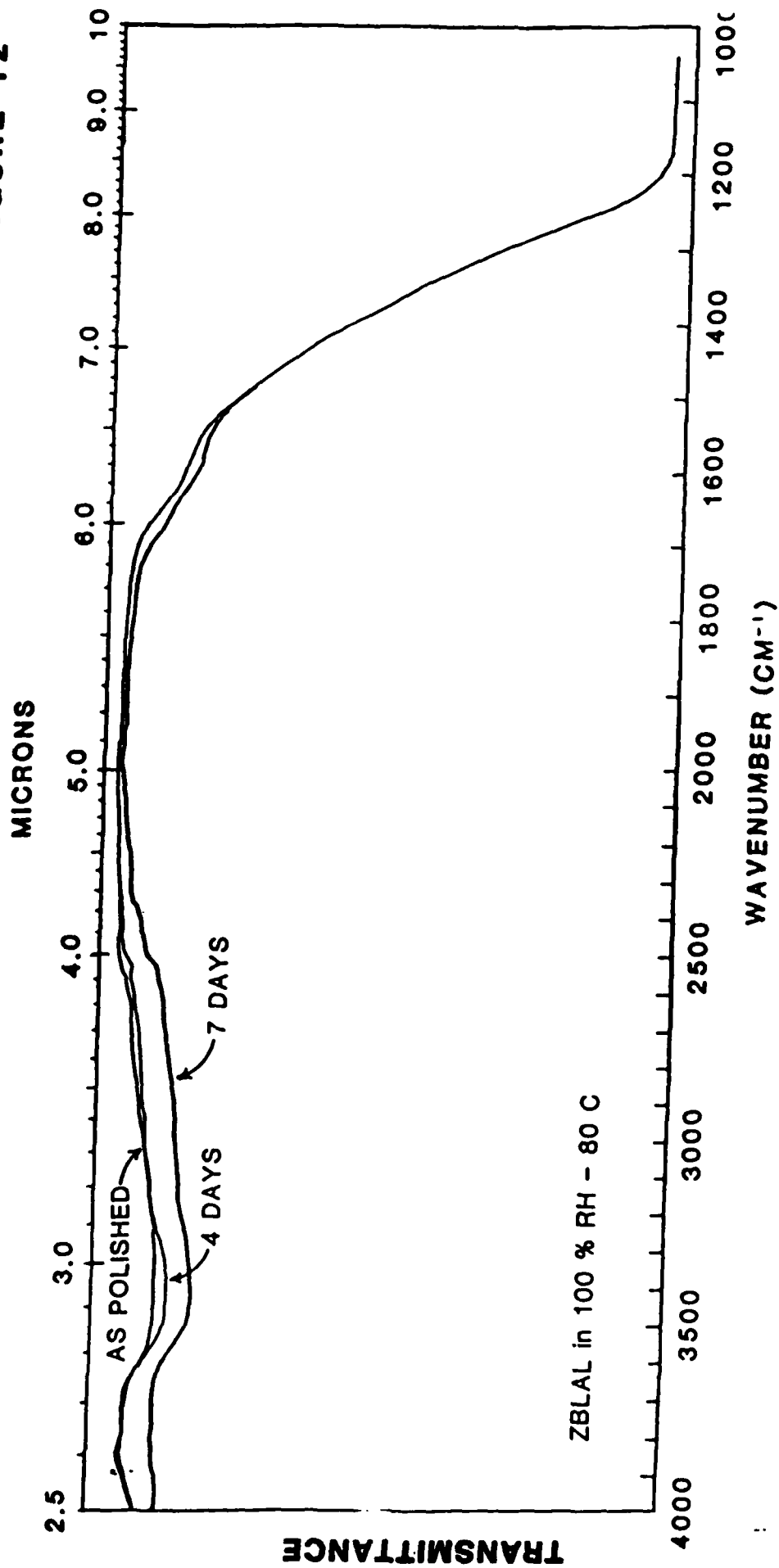
We conducted tests under 100% relative humidity conditions at 80°C for 7 days. Care was taken to maintain the sample temperature equal to that of the surrounding air in order to avoid condensation of water vapor. Visual observation of the sample (ZBLAL composition) showed no change in appearance over the test duration, and IR transmittance measurements confirmed less than a 5% loss between the before and after conditions of the sample (see Fig. 12).

It appears, therefore, that contact with an aqueous solution plays an essential role in the chemical corrosion process of these glasses.

#### c. Studies of Powder Samples

Solid samples are useful when surface studies (IR, SEM, SIMS) are to be conducted. However, due to the small exposed surface area, leachant concentrations in solution can be small (detection limit) and it is necessary to conduct leach tests for long time periods (30 minutes to 14 days depending on composition) and it is not possible to study the early stages of leaching behavior. These stages are of interest since they relate the behavior of the glass before the build up of surface deposits or a modified surface layer.

FIGURE 12



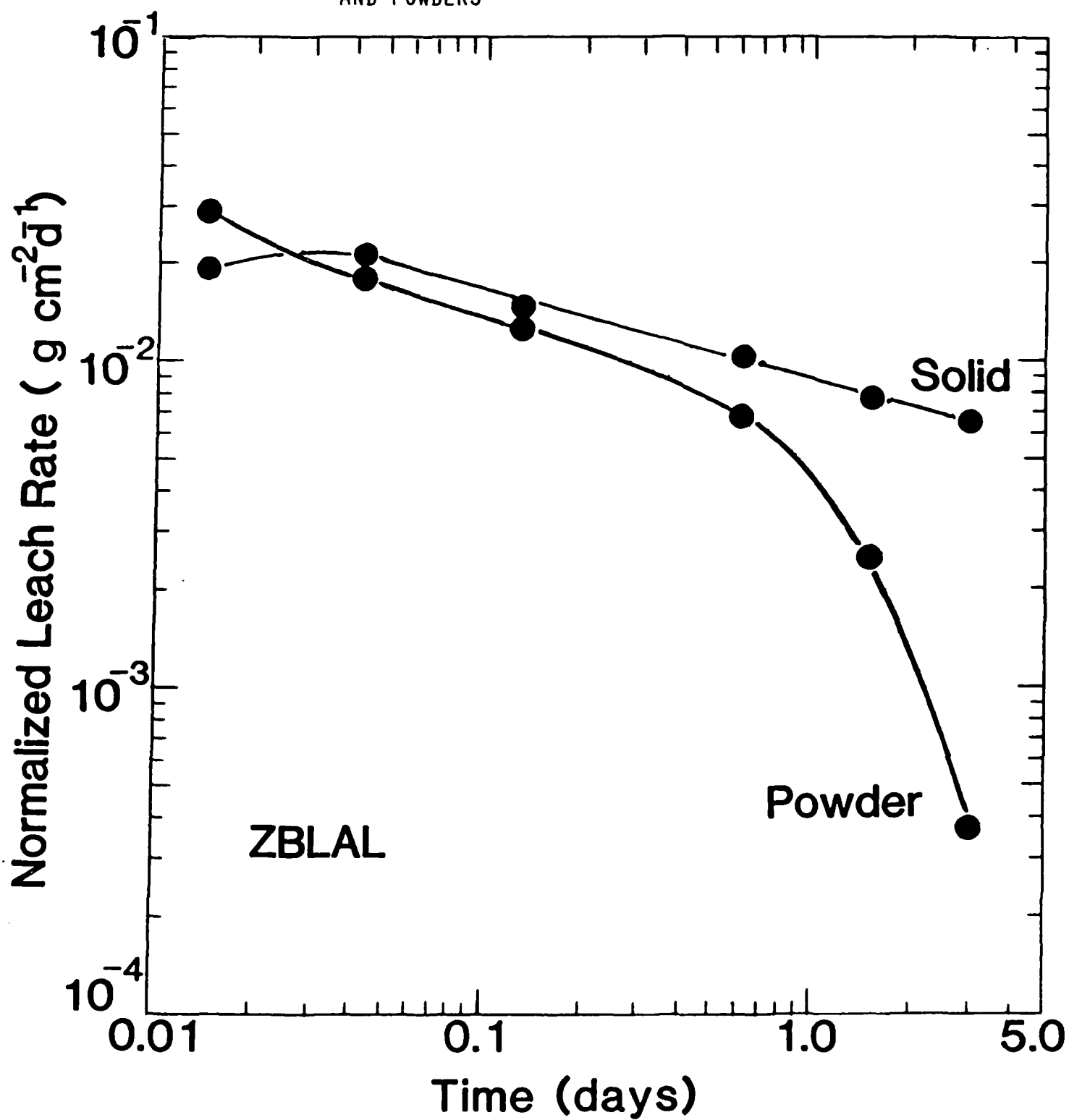
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Since the glasses in the  $\text{ZrF}_4$ -based family (Group I) exhibited similar leach rates and behaviors, we concentrated subsequent tests on a simple representative glass (ZBLAL).

A test was conducted on ZBLAL glass comparing the leach rates, as a function of time, of polished bulk samples with powdered samples (45-60 mesh) to confirm the surface area calculation for the powder. Figure 13 shows the results. At early times, the leach rates compare well and this confirms well the surface area calculation. The large reduction in leach rate observed at longer times for the powder samples, arises from the reduction in diameter of the powder resulting from the high leach rates. Therefore, powder samples are useful for short term tests, but the data must be corrected for surface area changes at longer times.

Six different tests were conducted on powdered samples. All the tests were conducted in a pH 2 buffer solution containing KCl and HCl. The test duration in each case was 15 minutes and the solution volume to surface area ratio was 10:1cm. Duplicate solution samples were analyzed for each test. In the first test, the powder was placed in the bottom of the PMP container and was allowed to stand for 15 min. The solution was decanted into 2 collection vials for analysis. Results (see Fig. 14) obtained on the DC Plasma Spectrometer show very poor agreement (shown by the error bars) between the 2 solutions due to incomplete mixing. Further, since the portion of the solution which had been in contact with the powder was not collected for analysis, the analysis data yielded a deceptively low value. Also if care is not taken, glass particles can be inadvertently collected with the solution for analysis, thus yielding a deceptively high value.

FIGURE 13 -- COMPARISON OF LEACH RATE FOR SOLID SAMPLES  
AND POWDERS





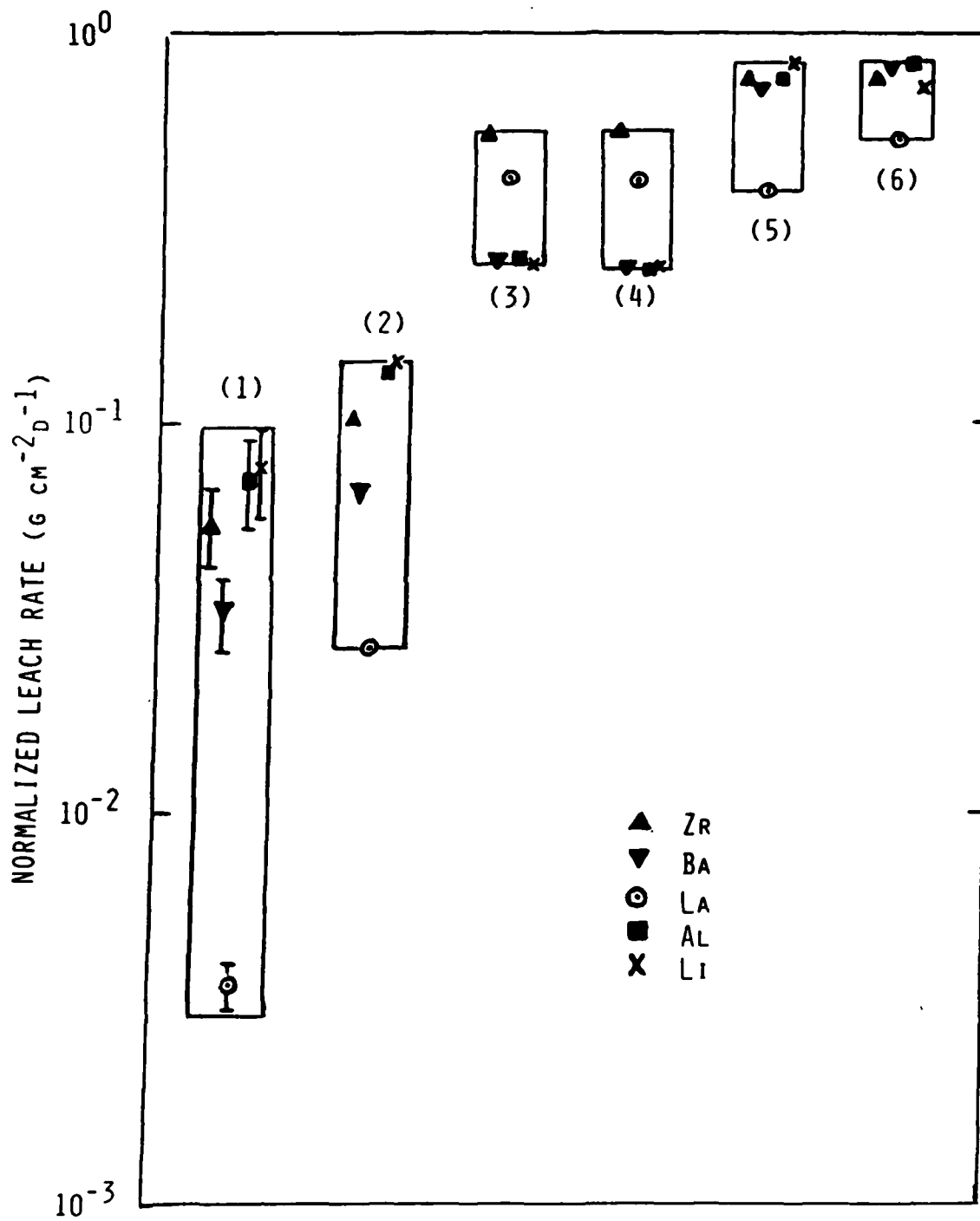


FIGURE 14 -- COMPARISON OF SEVERAL POWDER LEACH TEST CONDITIONS

In the second test, the sample and solution were poured through an analytical filter using an aspirator in order to collect the analysis solution. In this case the sample was well mixed and the duplicate samples of solution were in almost perfect agreement. The calculated leach rates were higher than in Test 1 by a factor of 2 except for La which increased by a factor of 7.

Tests 3 and 4 were conducted while the vial was exposed to ultrasonic agitation for 30 sec periods at the beginning and end. Test 3 was poured through a filter while test 4 was decanted. The results showed excellent agreement between duplicate samples within each test and no differences were found between the results of the 2 tests. Evidently thorough mixing was achieved by the ultrasonic agitation at the end of the test just prior to decanting. The data showed an increase by a factor of 6-20 in the leach rate, over the stagnant tests, with La exhibiting the largest increase.

Test 5 was conducted using constant rotation of the test cylinder at 50RPM. The data showed an increase in leach rate for all elements except La. This is thought to be due to constant mixing of the leachate in solution and the elimination of a transition layer in the solution at the glass surface where leachant products are concentrated and approach saturation. This data supports our conclusion as to the origin of the crystal precipitates observed on the surface of solid samples leached under stagnant conditions. It was suspected that the lack of change in the La leach rate from that of Tests 3 and 4 was due to a saturation of La in solution. Therefore, Test 6 was conducted as in Test 5, but with twice the solution volume (20:1 volume/surface). As expected, the La leach rate increased to a value within a factor of 2 of congruent dissolution.

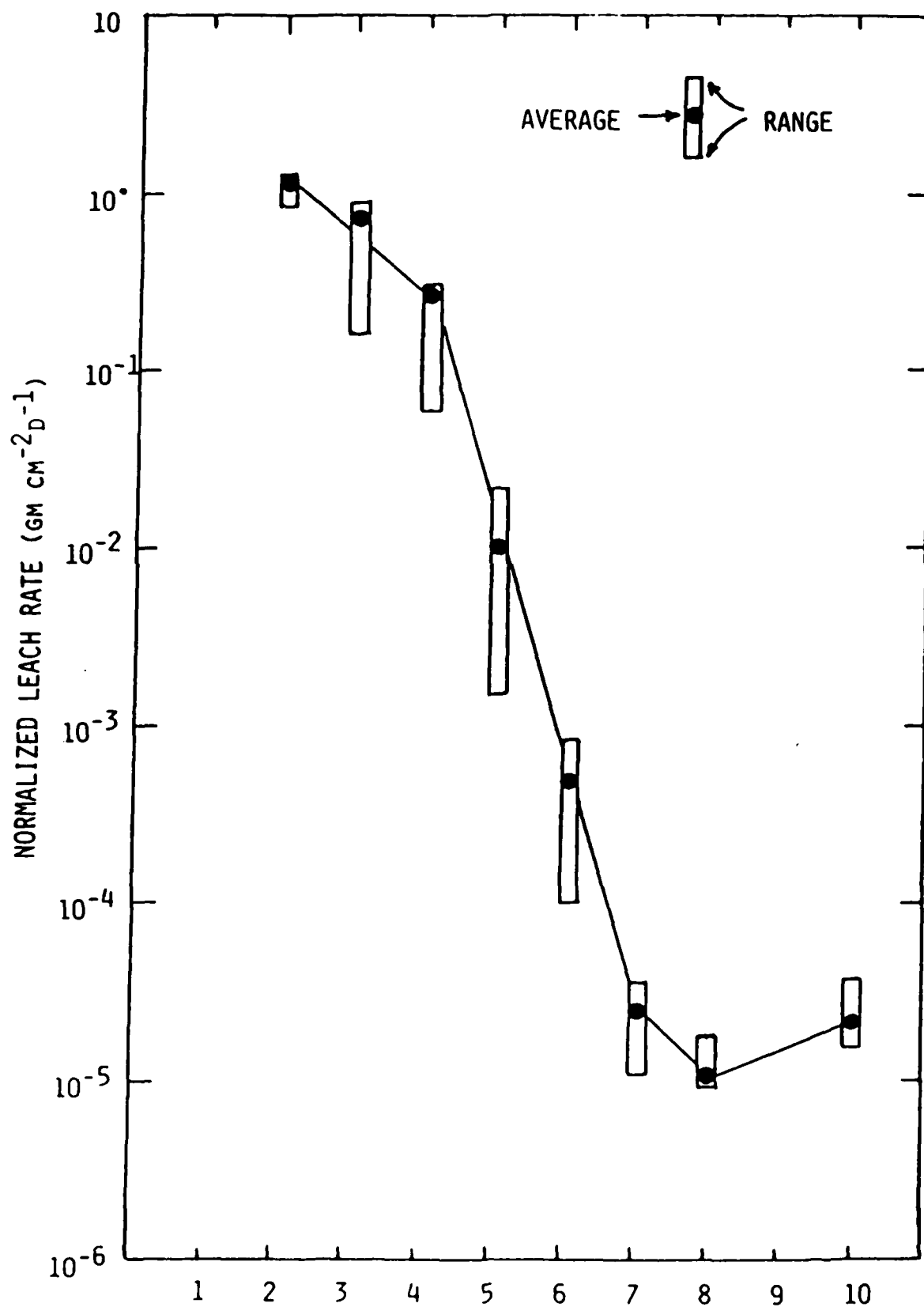
It is evident from these test results, that the test method exerts a large influence on the results obtained, and therefore, on the interpretation of the data. The conditions for Test 6 represent the closest simulation of high-dilution conditions where the influence of corrosion products is minimized. For this reason, all subsequent tests on powder samples were conducted using this method.

## 2. pH Studies on Zr-Fluoride Glasses

Tests in aqueous solutions at various pH values, in the basic and acidic range, were conducted on both solid samples and powders. The corrosion of the solid samples was monitored using IR transmission and microscopy. The corrosion of the powder samples was monitored using solution analysis. Some solution analysis was also attempted on the solid samples, however, in most cases, the leachates were below or near detection limits, especially at short soak times.

Tests were conducted in buffered solutions and in pH adjusted solutions. In the buffered solutions tests were conducted on 3 sets of samples in the range from pH 2 to pH 10. Duplicate tests were conducted at low pH (pH 2 to pH 5) using solutions whose pH was adjusted to the desired values using dilute HCl. The pH of the solutions was monitored at the beginning and end of the tests to confirm that it had not changed. Commercial buffers used were made from organic and inorganic components. The standards used for analysis were mixed using the same buffer solutions in order to match the matrix. The tests were conducted on powders prepared as described above, and leached in a vessel mixed by the constant rotation method described above. Results of solution analysis on a ZBLAL glass composition (see Table 1) are shown in Fig. 15.

FIGURE 15 -- pH DEPENDENCE OF LEACH RATE FOR ZBLAL GLASS



There appears to be an enormous pH dependence to the leach rate which is seen to decrease by 5 orders of magnitude between pH 2 and pH 10. Unlike the behavior of silicates which exhibits a minimum at neutral pH values and rises at both low and high pH, the fluoride glasses decrease monotonically as pH is increased. In fact at pH  $\approx$  8, their leach rate decreases to values only slightly above commercial silicate glasses. There appears to be a small increase in leach rate at pH 10. It is also interesting to note that, in the rolled-vessel, powder leaching tests, the differences in leaching between the individual glass components are not large.

IR transmittance spectra were obtained on solid samples. The extremes at pH 2 and pH 10.6 are shown and clearly demonstrate the effect of solution pH (see Fig. 16 and 17). The pH 2 data shows rapid corrosion of the surface with the formation of hydrates in a manner similar to the unbuffered neutral water tests. The pH 2 test shows a very rapid hydration of the surface as noted from a large absorbance in the bending and stretching vibrations of water. However, most of this water could be removed by drying overnight in vacuum at 98°C. This effective removal of water from the sample surface is different from samples leached in unbuffered de-ionized water, where the large hydration peaks could not be removed by drying.

In contrast, the sample immersed in pH 10.6 solution, containing  $\text{NH}_4\text{OH}$  shows relatively little sign of hydrate formation on the surface. However, an increase in absorbance over the entire spectrum occurs rapidly and appears to be due to surface scattering. Between 15 min and 20 hours of exposure, very little change was observed indicating some sort of passivating reaction. Figure 18 is an IR absorption graph taken from a sample immersed in a commercial pH 10 buffer solution for 13 days. Unlike the ammonia solution, no

FIGURE 16

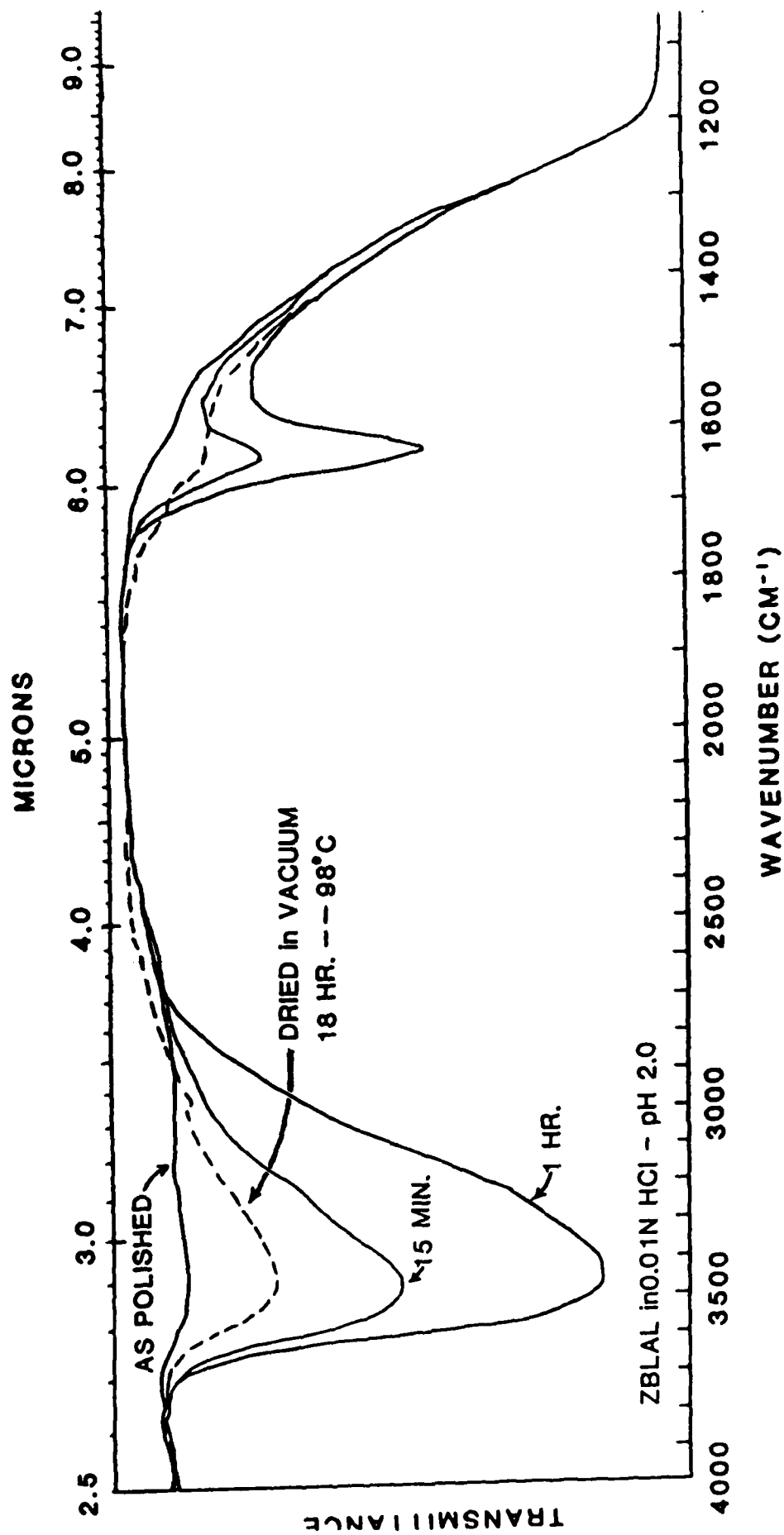
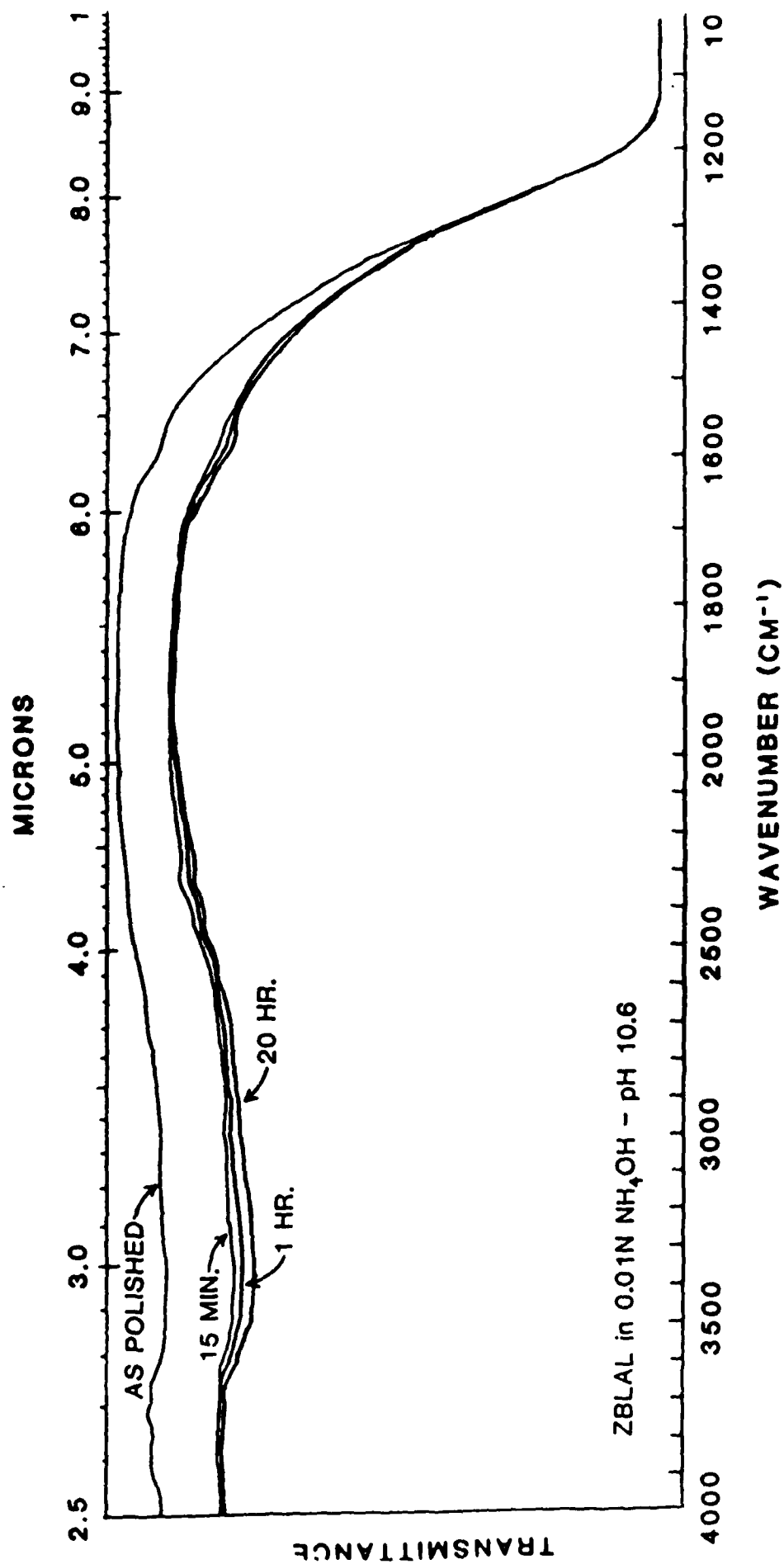


FIGURE 17



change was seen. The buffer solution contained  $K_2CO_3$ ,  $K_3BO_3$  and KOH. Figure 19 shows the spectra obtained for immersion in a NaOH solution of pH 10.3 for 13 days. Unlike the other two, absorption bands are clearly seen for the water vibrations indicating a surface hydration. These are still distinguishable after the sample was dried overnight in vacuum at 96°C.

The spectrum obtained for an immersion in a commercial pH 7 buffer solution for 14 days is shown in Fig. 20. Here we see a marked difference from the behavior of samples immersed in unbuffered de-ionized water. As with the buffered pH -10 test, very little corrosion of the sample has occurred.

Figure 21 from a pH 4 buffer test shows the absorbance of a sample which was immersed for 8 days. The sample was almost completely opaque and exhibited a spectrum with large hydration losses as in Fig. 22, along with a thick crystalline crust. Curve B shown in the figure corresponds to the transmittance of the sample after removal of the crust. The sample surface was extremely rough, however, the hydration peaks have disappeared from the spectrum, indicating that all the waters of hydration were incorporated in the crystalline crust. The observed loss appears to be due to light scattering from the surface.

### 3. Measurements on Other Glasses

A second family of fluoride glasses containing  $ThF_4$  and  $BaF_2$  as glass-formers was investigated. The compositions are shown in Table 1. Leach tests were conducted in the same manner as for the solid samples of  $ZrF_4$ -based glasses. The leach rates of the Thorium-Barium glasses in de-ionized water were 50-100 times lower than the  $ZrF_4$  glasses. Figures 23 and 24 show the leach data of individual components of BZYbT and BZYbTN glasses. In general,



FIGURE 18

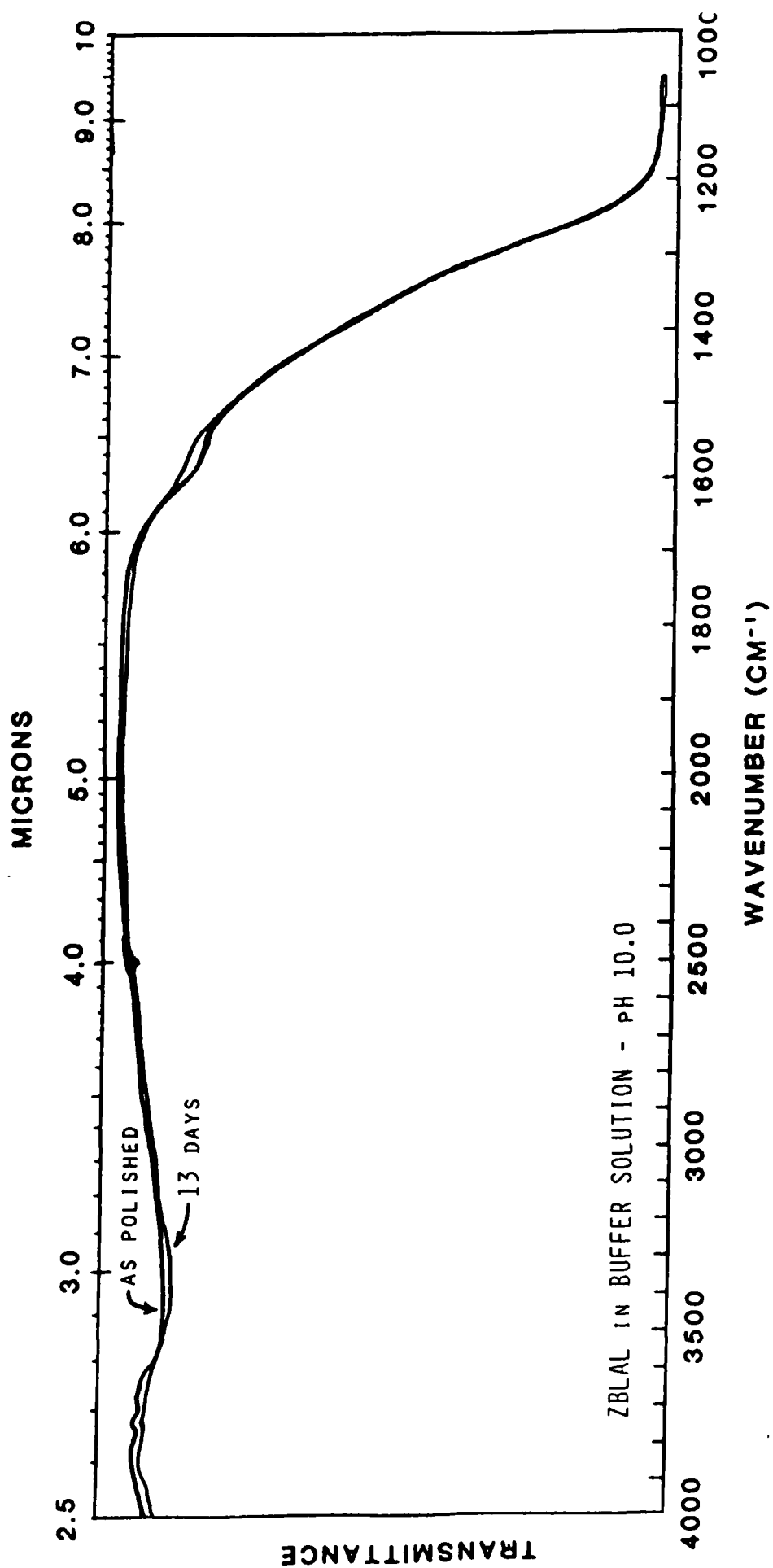


FIGURE 19

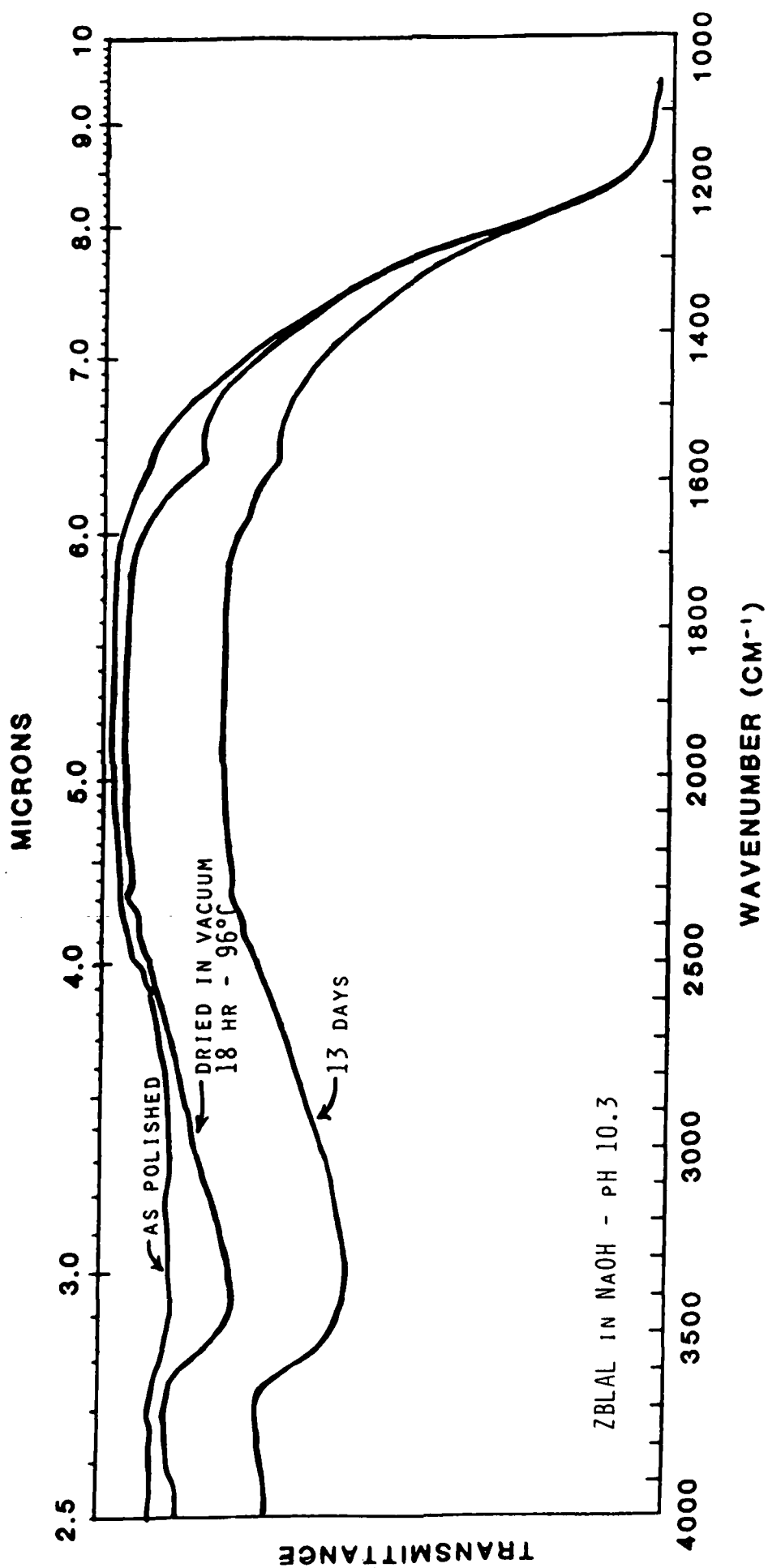


FIGURE 20

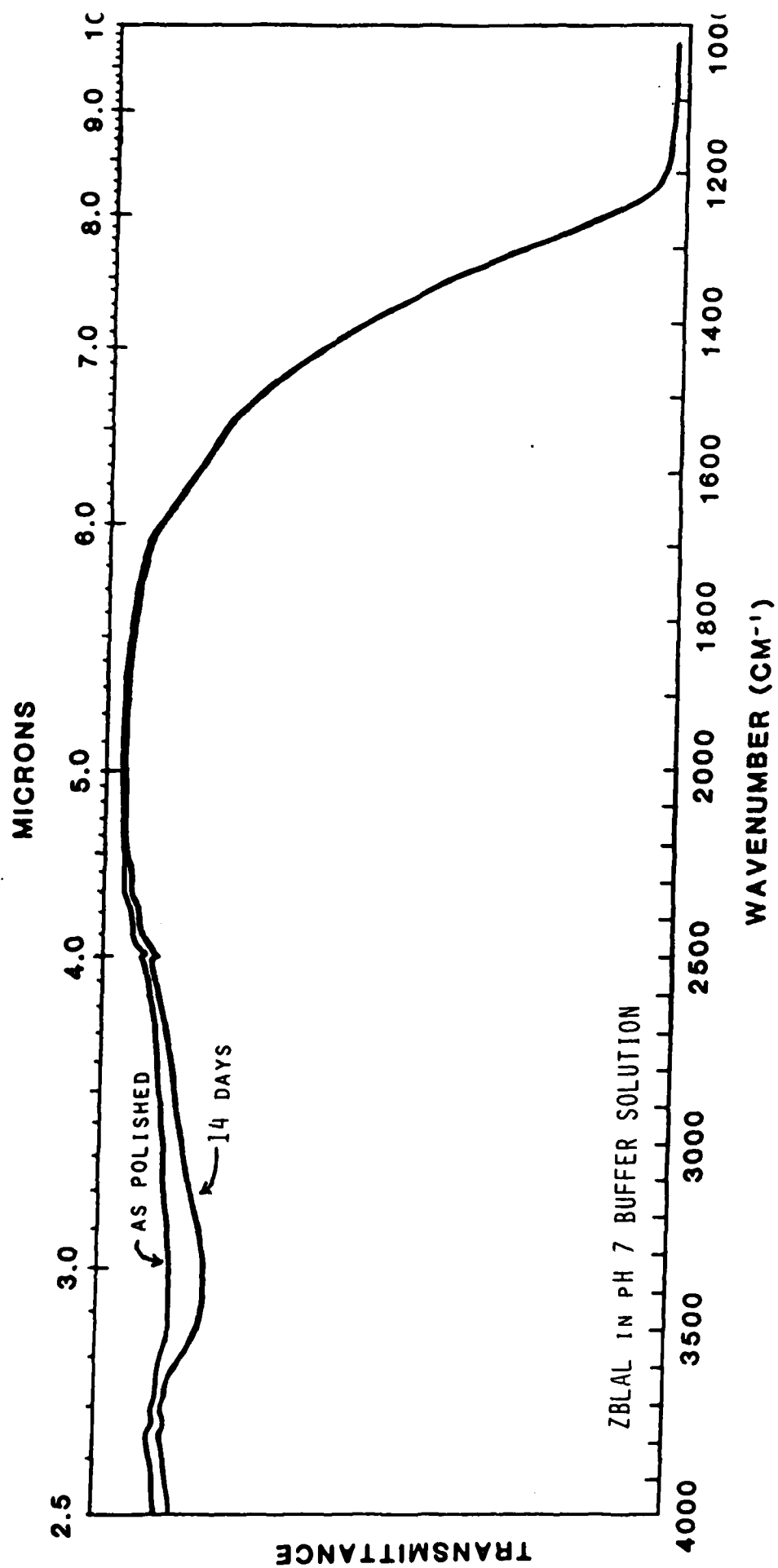


FIGURE 21

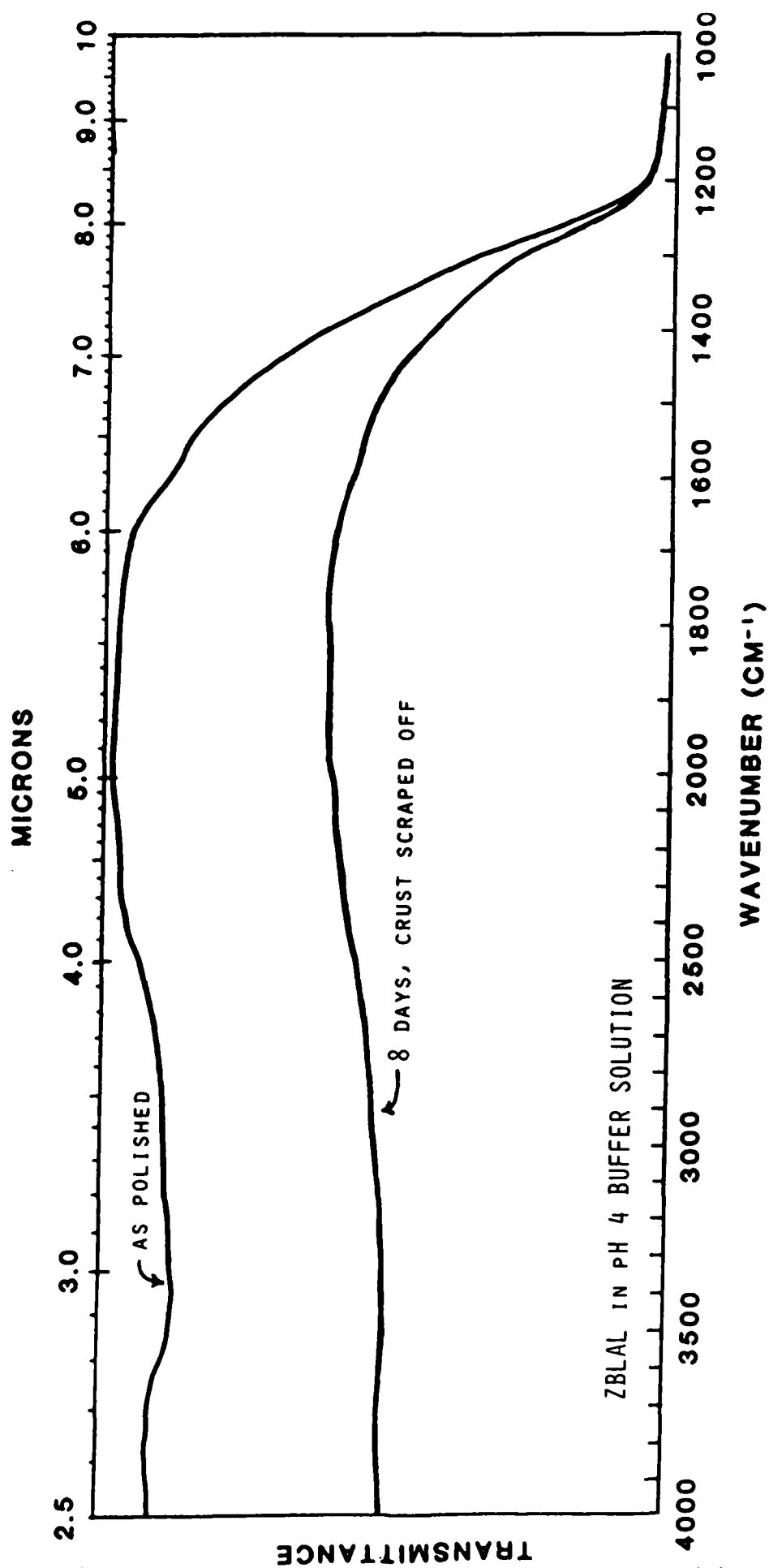
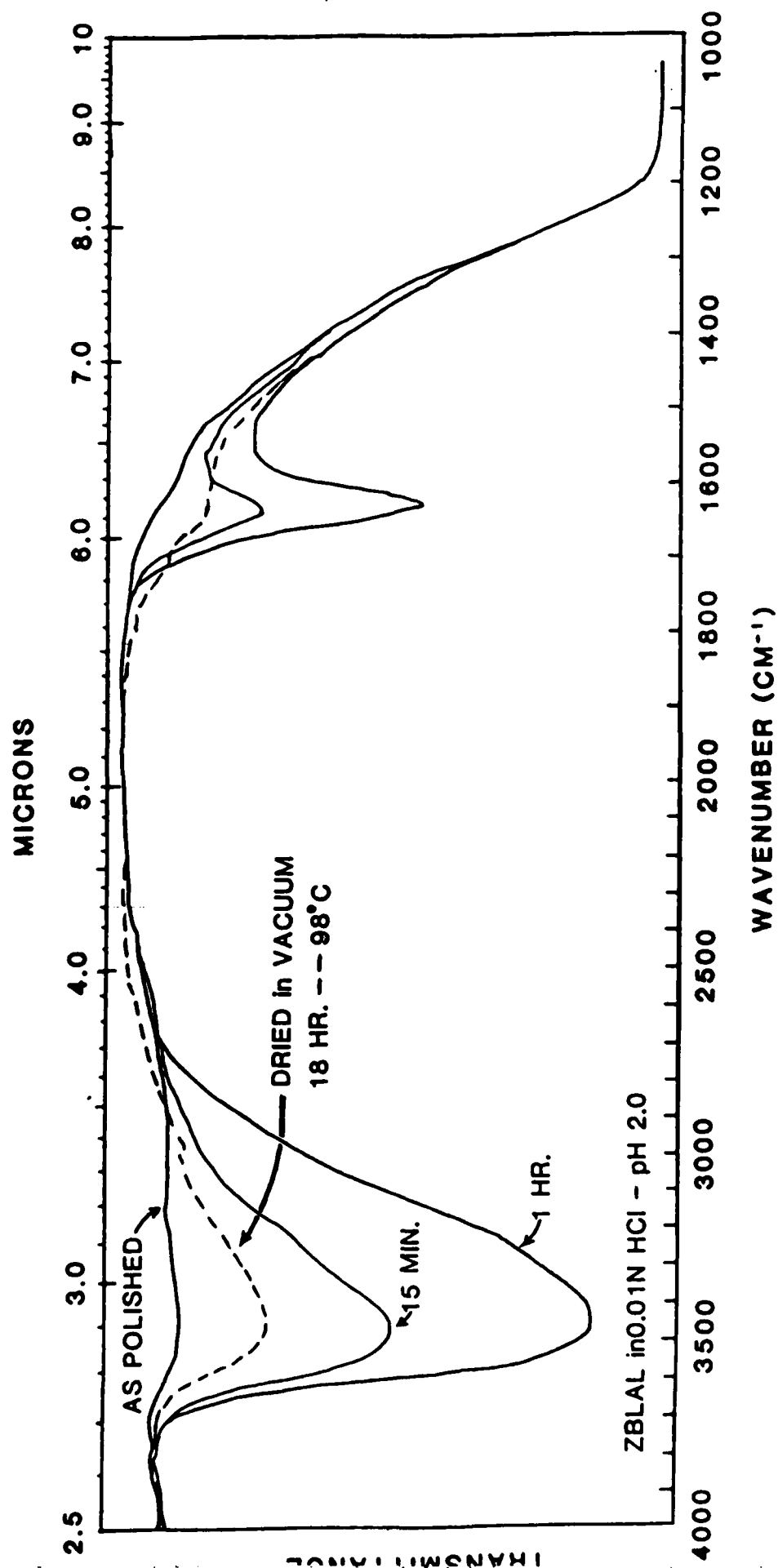


FIGURE 22



as for the  $ZrF_4$  glasses, the Th-Ba family of compositions behaved similarly, exhibiting approximately equal leach rates and relatively congruent leaching. The short time data shown on the curves was very close to detection limits and therefore has considerable uncertainty. Only a few analyses were possible for Th, again due to its presence in solution at levels near or below detection limits. In the BZYbTN glass, sodium is seen to leach at a rate above the other components and it follows a decrease with time reminiscent of silicate glasses. The pH drift of these samples in unbuffered de-ionized water, was less severe than seen in the  $ZrF_4$  glass family, reaching an equilibrium value of pH 4.8 instead of pH 2.46. Tests are presently underway on powdered samples in both de-ionized water and buffered solutions.

Figure 25 shows a comparison between the leach rates representative of the Th-Ba family and the  $ZrF_4$  family, along with leach rates of 2 alkali-silicate glasses and a commercial Pyrex glass.

The surface topography of leached samples was examined by scanning electron microscopy. Once again, samples within Group I or II were very similar to one another in the extent of attack and type of surfaces formed. Elements contained in the crystal deposits on the surfaces were identified by x-ray analysis using a wavelength dispersive spectrometer and are listed in Table 3. Whereas the Zr/Hf glasses had developed a thick, hydrated surface layer, overlaid by a crystalline crust, and were quite opaque after 5 days of exposure, the Th-Ba glasses appeared to have suffered much less damage and were still fairly transparent. The thickness of these crusts was determined by SEM to be  $> 150\mu m$  for the Group I glasses and  $\sim 2-3\mu m$  for the Group II glasses. This ratio is in good agreement with the leach rate data.

FIGURE 23

Normalized Leach Rate ( $\text{g cm}^{-2}\text{d}^{-1}$ )

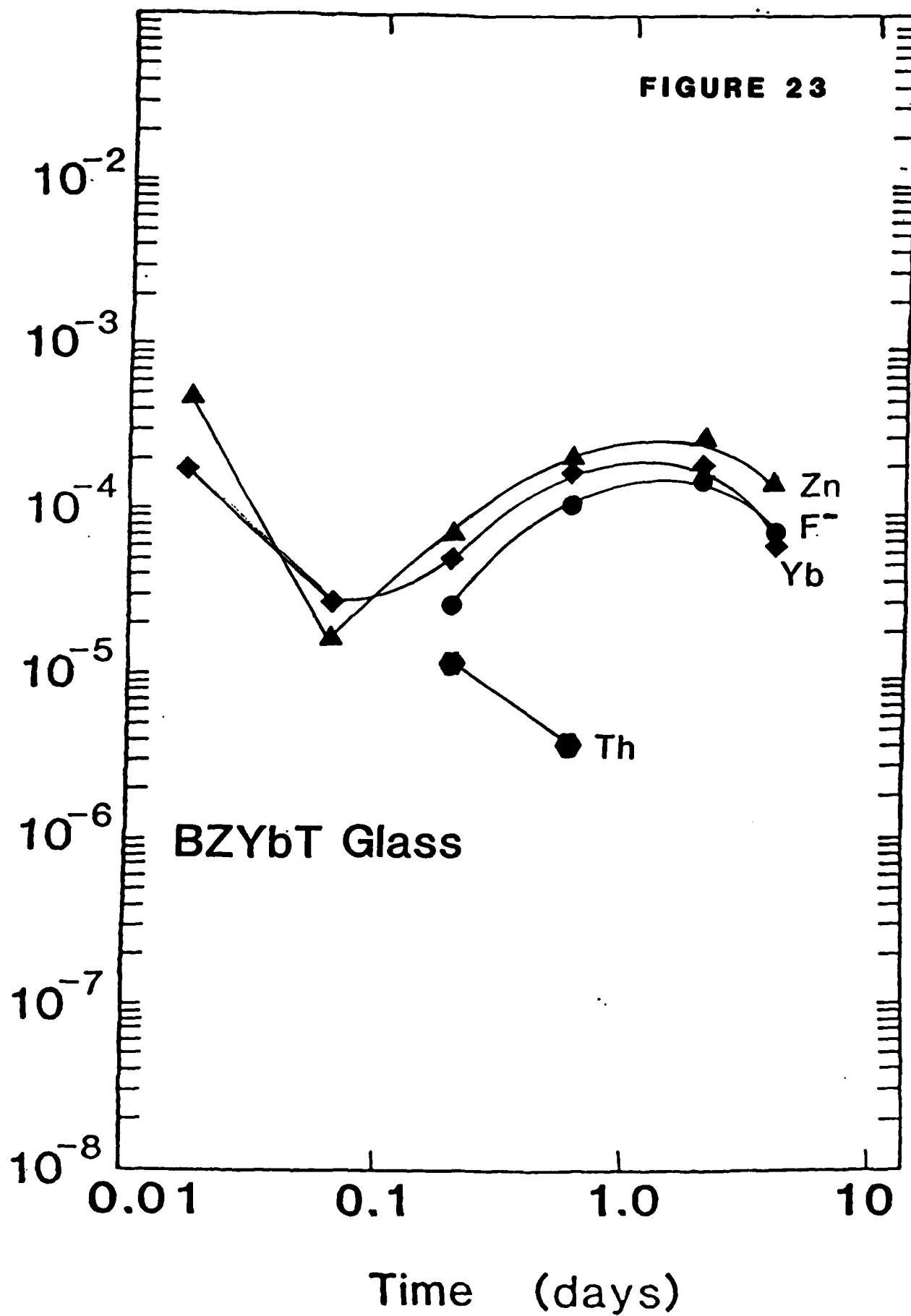


FIGURE 24

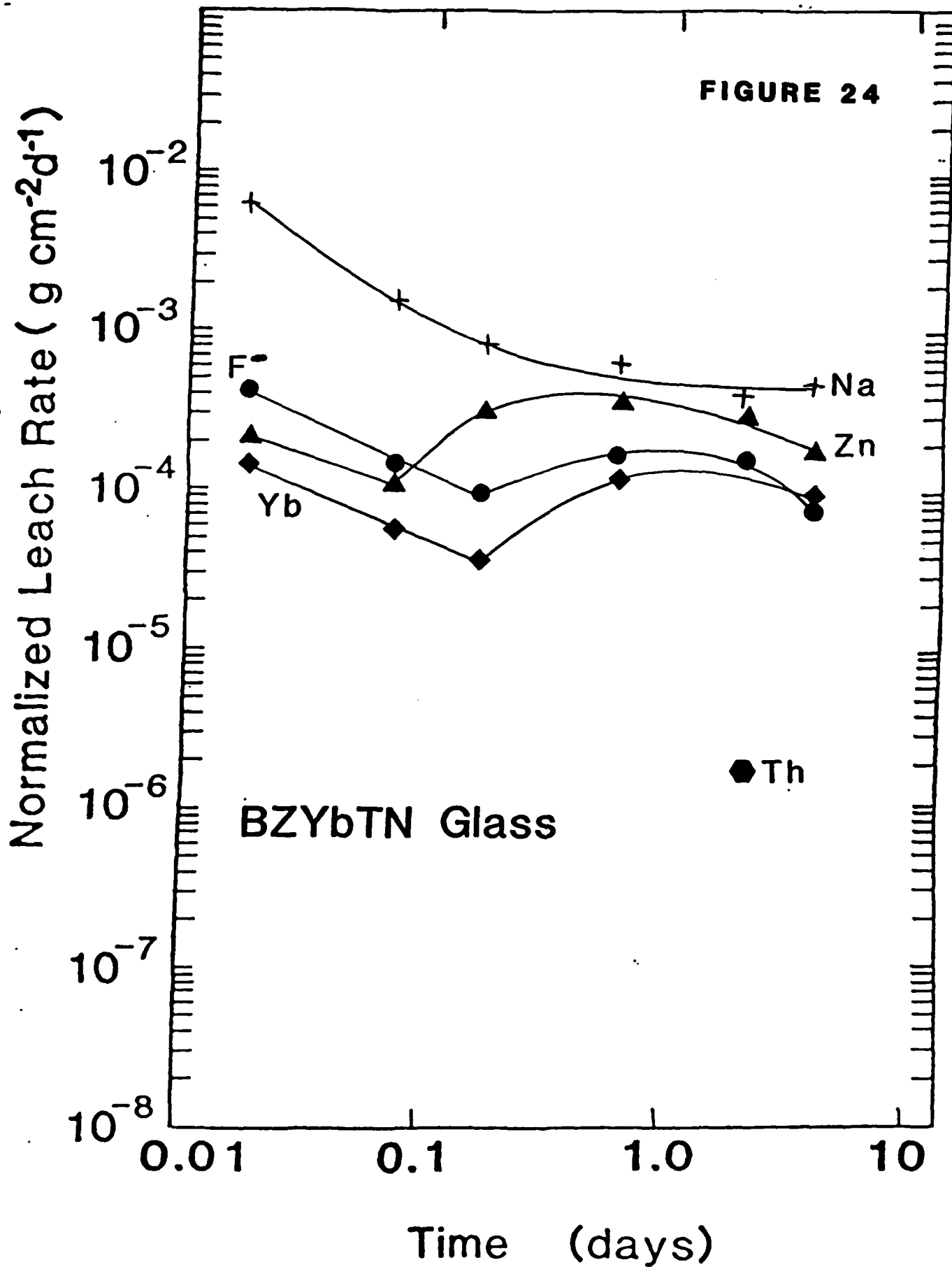




FIGURE 25

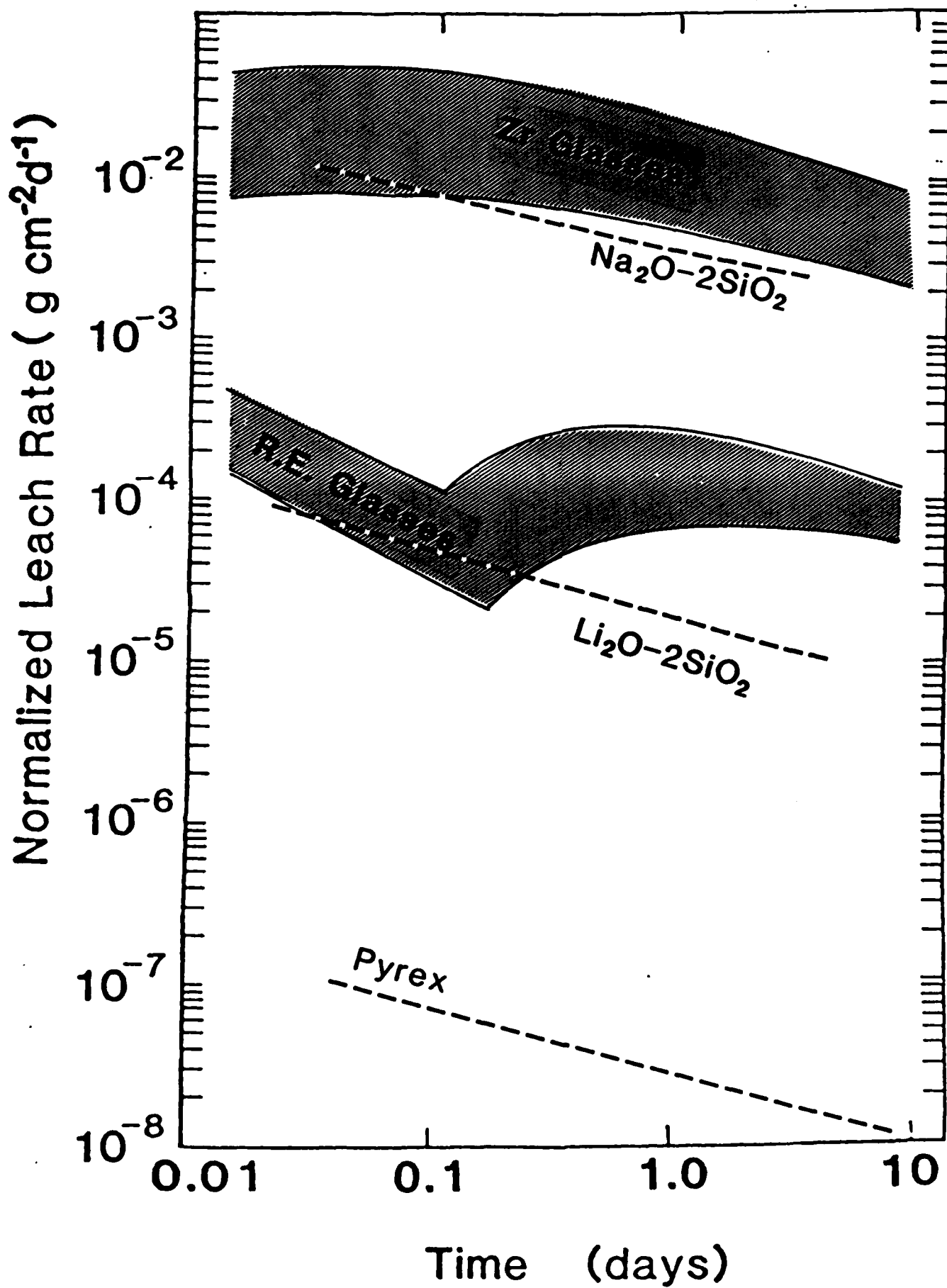


Table 3. Summary of Observations in Composition Study

Type	Leach Rate g/cm <sup>2</sup> day	Sample Surface	Crust Thickness	Crystals Identified
Group I	10 <sup>-2</sup>	Opaque	150μm	Zr, Ba, La
Group II	10 <sup>-4</sup>	Frosted	3μm	Ba, Yb, Th

### C. Interpretation of Results

In combining together the data presented in the previous section, a model for the corrosion of fluoride glasses begins to emerge. At this point in the research, this is still a somewhat tentative model, but the pieces appear to be coming together consistently. The research being conducted and planned for next year's program is designed to test the emerging conclusions, strengthen the model and increase the detail.

The pH dependence study has supplied the most important conclusion to date. It appears that the solubility of  $ZrF_4$  in solution directly controls the corrosion rate of the glass. In solutions of various pH values it is the chemical form of the Zr compounds ( $ZrF_4$  vs  $ZrO_2$  vs  $ZrO_xF_y$ ) and its solubility which controls the corrosion rate. At high pH values the  $ZrF_4$  on the glass surface reacts to form  $ZrO_2$  which is insoluble. This reaction leads to the formation of an insoluble layer on the glass surface which effectively protects it from further corrosion, in high pH solutions. This is clearly evident in the IR transmission data where only an increase in optical scattering is visible and the large surface hydration peaks seen at lower pH values are completely absent.

A test was conducted to examine this premise. In this test a sample of ZBLAL glass was immersed for 10 days in a pH 10 solution and the protective  $ZrO_2$  layer was allowed to form. Afterwards, the sample was immersed in de-ionized water at pH 5.8 solution. Subsequent solution analysis showed that the leach rate went back to the behavior of untreated ZBLAL samples, however, this only occurred after an incubation period of 1 day where the sample remained in the pH 5.8 solution without exhibiting any noticeable corrosion.

At low and neutral pH values the solubility of  $\text{ZrF}_4$  is relatively high (as shown by preliminary measurements to be confirmed in next year's work) and the glass is corroded nearly congruently through the dissolution of its  $\text{ZrF}_4$  matrix. The  $\text{BaF}_2$ ,  $\text{NaF}$ ,  $\text{LiF}$  and  $\text{AlF}_3$  solubilities are all sufficiently high to allow this dissolution to occur without any significant hindrance. Analysis of dissociated fluoride in solution by the Dionex ion analyzer or the Fluoride electrode methods shows too little  $\text{F}^-$  in solution to account for the dissolved metal cations analyzed in the DC Plasma spectrometer. This result clearly rules out any major ion exchange process in the glass similar to that seen in silicate (oxide) glasses. More importantly, this result indicates that a significant amount of fluoride remains strongly complexed in solution and evades detection by analysis.

In neutral solutions the leaching behavior is more complicated by the lack or presence of buffering agents. In the unbuffered de-ionized water test, first reported, there appears to be a moderate ion exchange of  $\text{F}^-$  for  $\text{OH}^-$ , possibly on the Ba and La precipitates. This exchange lowers the pH into the acidic range, thus increasing catastrophically the  $\text{ZrF}_4$  dissolution and the glass corrosion. The solution pH continues to decrease until it reaches a value near 2.46. In buffered neutral pH solutions, there is no appreciable decrease in solution pH and the glass corrosion rate is much lower.

Deposits on the surface appear to come from the very slow mixing of leachates with the solution in the absence of continuous agitation (as seen in the powder tests reported above, and also reported by Pantano<sup>12</sup>). As  $\text{ZrF}_4$  dissolves from the glass, the solution adjacent to the glass surface rapidly reaches saturation and precipitates the needle-like  $\text{ZrF}_4$  crystals commonly seen on the surface of these glasses when immersed in water. Ba crystals have also

been observed as described earlier. Future x-ray studies will help determine their chemical make-up. Electron micrographs have also shown that in low pH or unbuffered de-ionized water solutions, the surface of the glass suffers acute hydration and cracks without the formation of any cohesive protective layer.

A comparison of the leach rates of the family of  $\text{ZrF}_4$ -based glasses with the  $\text{ThF}_4$ -based glasses indicates that the  $\text{ThF}_4$  matrix is less easily attacked by water. We expect that this effect is due to a lower solubility of  $\text{ThF}_4$  in water. In this case, however, the solubility may be low enough, that the matrix weakening process is occurring through the Ba instead. If this were the case, the leaching mechanism of  $\text{ThF}_4$ - $\text{BaF}_2$ -based glasses may be quite different from  $\text{ZrF}_4$ -based glasses. An investigation of the pH dependence of  $\text{ThF}_4$ -based glasses is underway and promises to elucidate this question.

Finally, tests in air of relatively high humidity differ strikingly from aqueous immersion tests because of the inability of unprecipitated humid air to dissolve  $\text{ZrF}_4$  from the glass. Major hydration of the surface is only observed if moisture is allowed to precipitate on the glass surface. Since ion exchange plays a relatively minor role in the chemical corrosion of the  $\text{ZrF}_4$  glasses, they will not exhibit the colorful appearance of weathered ancient soda-lime silica glass windows and bottles.

#### IV. Conclusions

Fluoride glasses offer a new group of materials whose applications are very promising in optical communications and general optics, but whose behavior is very complex. Since their structure of ionically bonded metal-halide groups is drastically different from the silicate glasses with covalently bonded  $\text{SiO}_4$  tetrahedra whose structure is determined by their bridging oxygen bonds, it is

not surprising to find that the behavior of these halide glasses differs drastically from that of silicate glasses.

The low chemical durability of halide glasses appears to be the major flaw hindering their widespread use. Because of the stated differences from silicates, it was not possible to extend the vast knowledge and experience accumulated for silicate glasses over the past 50 years. Therefore, chemical corrosion mechanisms had to be investigated from early stages. Using our past experience of chemical durability tests on nuclear waste glasses, we were able to apply rigorous testing techniques, and accurate analysis techniques to the problem. At present, a model for understanding the corrosion behavior of halide glasses has emerged and taken shape. With further testing and access to surface and x-ray analysis equipment, we expect to verify the model and increase the detail in our understanding of the underlying principles of chemical corrosion. As the work progresses, we expect to be able to lay the ground work for a scientific guidance in the choice of useful halide glass materials and in the determination of their expected behavior under various field conditions.

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